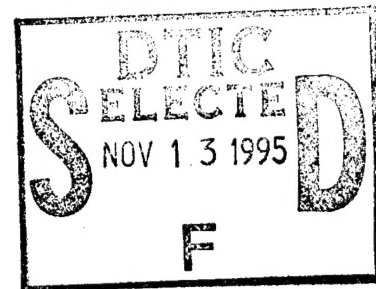


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FINAL REPORT
BY
MEMBRANE SYSTEMS, INC.

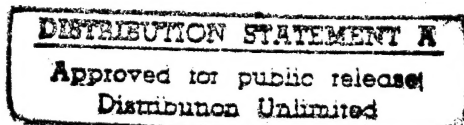


TO
OFFICE OF WATER RESEARCH AND TECHNOLOGY

CONTRACT NO. 14-34-0001-8523

SEPTEMBER 1979

DEVELOPMENT OF
REVERSE OSMOSIS MEMBRANE
FOR
SEAWATER
DESALINATION



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-- 1 - AD NUMBER: D432160
-- 5 - CORPORATE AUTHOR: MEMBRANE SYSTEMS INC SAN DIEGO CA*
-- 6 - UNCLASSIFIED TITLE: DEVELOPMENT OF REVERSE OSMOSIS MEMBRANE FOR
-- SEAWATER DESALINATION.
-- 9 - DESCRIPTIVE NOTE: FINAL REPT.,
--10 - PERSONAL AUTHORS: BOTT,J. B. ;FOX,R. L. ;GAGHER,S. J. ;MCKEE,M. E. ;
-- SUDAK,R. G. ;
--11 - REPORT DATE: SEP , 1979
--12 - PAGINATION: 114P
--15 - CONTRACT NUMBER: DI14-34-0001-8523
--20 - REPORT CLASSIFICATION: UNCLASSIFIED
--22 - LIMITATIONS (ALPHA): APPROVED FOR PUBLIC RELEASE; DISTRIBUTION
-- UNLIMITED. AVAILABILITY: MEMBRANE SYSTEMS INC., 11111 FLINTKOTE AVE.
-- , SAN DIEGO, CA. 92121.
--33 - LIMITATION CODES: 1 24

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TABLE OF CONTENTS

| | <u>Page</u> |
|--------------------------------------|-------------|
| I. INTRODUCTION | 1 |
| II. MSI-400 MEMBRANE SERIES | 5 |
| A. Introduction | 6 |
| B. Modified Small Scale Optimization | 13 |
| C. Continuous Casting | 30 |
| D. Spiral Wound Element Fabrication | 40 |
| E. Program Summary | 51 |
| III. MSI-500 MEMBRANE SERIES | 53 |
| A. Introduction | 54 |
| B. Research Program | 59 |
| C. Program Summary | 73 |
| IV. MSI-600 MEMBRANE SERIES | 76 |
| A. Introduction | 77 |
| B. Research Program | 80 |
| C. Program Summary | 97 |
| V. POROUS SUPPORTS | 99 |
| A. Introduction | 100 |
| B. Research Program | 100 |
| C. Program Summary | 112 |

I. INTRODUCTION

Work under OWRT Contract No. 14-34-0001-8523 was initiated in July 1978 and completed in September 1979. The major objective of the contract was the development of reverse osmosis membranes with the capability of converting seawater to potable usage. The work was divided into 4 programs as follows:

- A. A membrane barrier layer formed by the interfacial polycondensation of polyethylenimine and isophthaloyl chloride.
- B. A membrane barrier layer formed by the interfacial polycondensation of poly(epichlorohydrin-secondary diamines) and diacid chlorides.
- C. An asymmetric polyimide membrane.
- D. Optimization of porous substrates for composite membranes.

The membrane barrier layer formed from polyethylenimine/isophthaloyl chloride was first investigated at Membrane Systems under OWRT Contract No. 14-34-0001-7513. The primary objective of that contract was the development of a low pressure (250 psig) membrane for the desalination of brackish waters. Following successful completion of a laboratory phase and small element development phase, this membrane was incorporated into 4 inch diameter spiral wound elements. Six of these elements were subjected to testing at the OWRT Test Facility at Roswell, New Mexico in March 1979. As of September 1979, these elements had been under test for 4,000 hours with a flux of 20 GFD when operated on a feedwater containing about 3,000 mg/l TDS at 250 psig and 75°F. Based on the average of the concentrations of the feed and reject, the rejection was 97.4% with a recovery of 24%. Since this membrane barrier layer

had shown promise in reducing the energy costs of brackish water desalination, it was proposed that an investigation be undertaken to determine its potential for seawater desalination.

The major thrust of OWRT Contract No. 14-34-0001-8510 was the development of a composite membrane which is resistant to attack from residual chlorine. This work was undertaken in May 1978 and completed in May 1979. It has been hypothesized that the cause of residual chlorine attack on polyamide membranes is due to the presence of secondary amines in the membrane barrier layer polymer. By synthesizing a prepolymer from polyepichlorohydrin and secondary diamines such as piperazine, and further reacting this prepolymer with diacid chlorides, the secondary amines have been eliminated. While not being totally resistant to residual chlorine, a composite membrane was prepared and it exhibited acceptable performance under low pressure, brackish conditions. Additional work was undertaken under the contract covered by this report to optimize the membrane for seawater conditions.

The secondary objective of OWRT Contract No. 14-34-001-8510 was to develop porous substrates for composite membranes which would provide a broader degree of tolerance to solvents and accomodate higher temperatures. During this investigation, a hydrophilic polyimide porous support was developed for composite membrane application. Further development yielded an asymmetric polyimide membrane for reverse osmosis application. Within the constraints of time, additional development of this membrane under the contract covered by this report was undertaken.

Composite membrane development to date has been largely based on the use of a polysulfone porous support and this development has been impeded by the lack of appropriate fabric carrier materials. The work reported herein was centered on improvement of polysulfone porous supports and identification of problems encountered with commercially available fabric carrier materials.

II. MSI-400 MEMBRANE SERIES
POLYETHYLENEIMINE-ISOPHTHALOYL CHLORIDE

A. INTRODUCTION

The most popular sheet membrane in use today is an asymmetric cellulose acetate consisting of a relatively dense layer (0.2 microns) and a porous layer (99.8 microns). An obvious extension of this is the concept of a composite membrane which has a membrane barrier formed on a porous support cast on a carrier fabric.

Fabric carrier materials used in composite membranes have been either a woven dacron or a non-woven polyester, both demonstrating equally good results. The choice between the two rests on mechanical properties and economic considerations as the chemical nature of the fabric seldom contributes to, or detracts from, the desalination properties of the composite membrane.

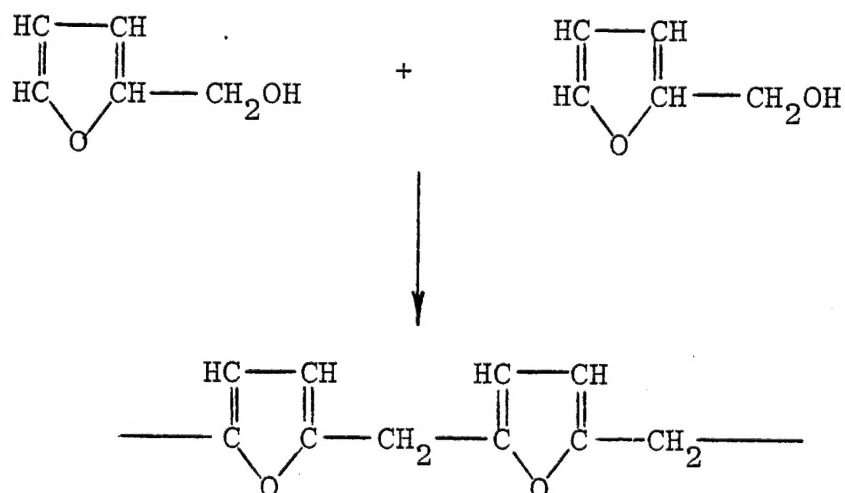
Several polymers have been used as porous supports. Cellulose nitrate-cellulose acetate was used with a dip-coated cellulose triacetate film. Although this was considered a technical success in the desalination of seawater, this porous support material is expensive to produce and difficult to handle. Most recently, the predominant porous support material used in composite membranes has been polysulfone. This material has been the most successful among the limited number of polymer systems investigated as porous supports, but it does have limitations in temperature and solubility. Consequently, other materials which will allow barrier membrane formation at

higher temperatures or from a broader choice of solvents are under investigation.

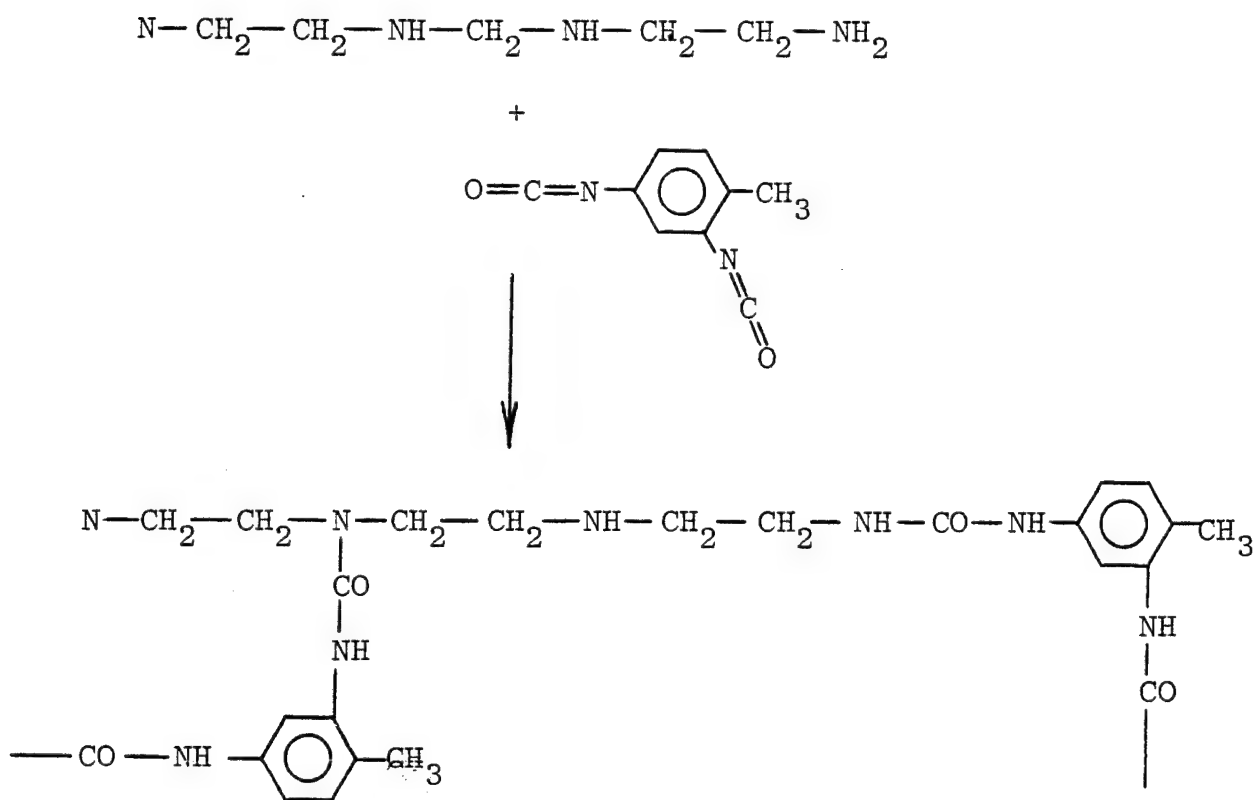
Membrane barriers have been formed on porous supports in various manners including the following:

1. Solution Coatings, e.g., the cellulose triacetate discussed above.
2. Thin Film Polymerization, e.g., the NS-200 membrane discussed below.
3. Interfacial Condensation, e.g., the NS-100 membrane discussed below.

The NS-200 membrane, a furan resin derived from the monomer furfuryl alcohol, is an example of in-situ thin film polymerization. The polymer is formed under strongly acidic conditions. The reaction is checked by cooling and proper neutralization to higher pH. The polymerization is an inter-molecular dehydration with a linear molecular structure as follows:



The NS-100 membrane is an example of a composite membrane formed through interfacial condensation. The polymer barrier is formed by a condensation reaction at the interface of an aqueous and organic phase. The aqueous phase contains polyethyleneimine while the organic phase contains toluene diisocyanate. The reaction proceeds in the following manner:



Polyethyleneimine will readily react with a variety of organic reagents and another membrane (PA-100) has been successfully formed by reacting it with isophthaloyl chloride. A membrane commonly referred to as PA-300 is formed by the

reaction of epiamine and isophthaloyl chloride. Another, known as RC-100, is formed with epiamine and toluene diisocyanate. Reaction conditions dramatically influence the resultant reverse osmosis properties of all the above membranes.

Under OWRT Contract No. 14-34-0001-7513, Membrane Systems, Inc. demonstrated that the reverse osmosis properties of the membrane formed by interfacial condensation between Dow polyethyleneimine-1000 (PEI) and isophthaloyl chloride (IPC) can be altered by varying the concentration of the reactants. It was also shown that the acid acceptor, a component in the reaction mixture, influences the characteristics of membrane barrier layers. In the course of work accomplished under that contract, a membrane (MSI-400) was produced with a flux of 20 GFD and a rejection of 97% when operated at 250 psig on a feedwater containing 5000 mg/l NaCl.

Both polycarbonate and polysulfone were utilized as successful porous support materials. Polysulfone film was cast from a solution of dimethylformamide and bis(2methoxyethyl) ether. The polycarbonate porous support film was cast from a dimethylformamide solution with no additives.

A non-woven fabric carrying material was used in all experiments. It is felt that the non-woven fabric has definite economic advantages over a woven fabric.

Using the interfacial PEI/IPC membrane optimized for brackish water, preliminary work was done to optimize it for seawater applications. One membrane layer formation variable,

IPC concentration in the organic phase of the interfacial condensation, was investigated. Under test between 500 and 1000 psig with a feedwater containing 34,200 mg/l NaCl at 75°F, a membrane made with 0.6% IPC demonstrated the properties shown in Table II-1 and Figure II-1. As can be seen, potable water was produced at pressures of 700 psig and above. At these pressures, the membrane also produced respectable fluxes.

The first objective of OWRT Contract No. 14-34-0001-8523 covered by this final report was to optimize the formation of the modified MSI-400 membrane barrier layer to improve flux and rejection at 800 psig on a laboratory scale and then to produce comparable membrane on the large scale interfacial applicator machine. The performance goal was 20 GFD and 99.5% rejection at 800 psig and 75°F on a feedwater containing 35,000 mg/l NaCl.

TABLE II-1

PERFORMANCE OF MODIFIED MSI-400 MEMBRANE
AS A FUNCTION OF PRESSURE
34,100 mg/l NaCl 75°F

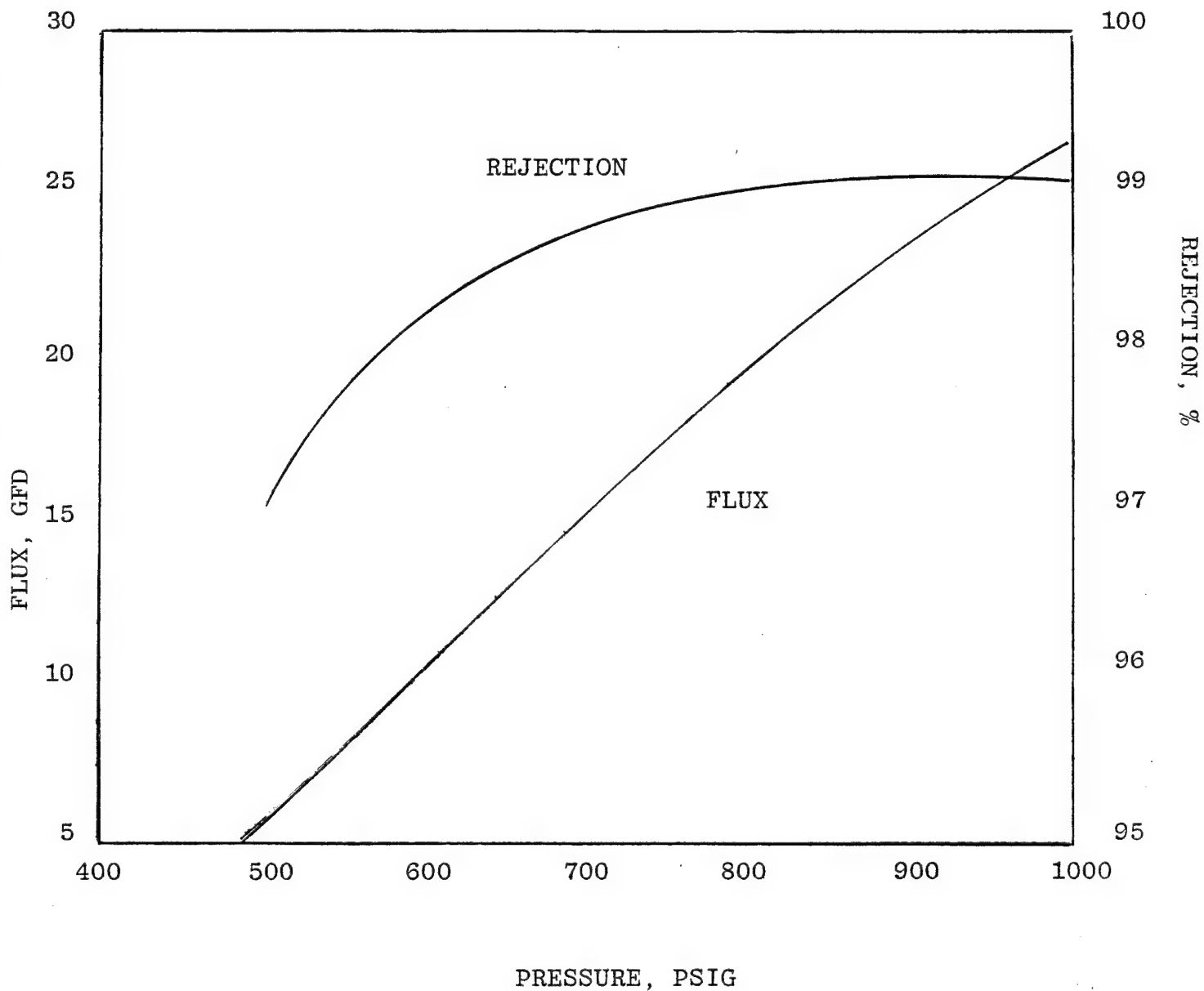
| <u>PRESSURE, PSIG</u> | <u>PRODUCT CONCENTRATION, PPM</u> | <u>REJECTION, %</u> | <u>FLUX, GFD</u> |
|---------------------------|---------------------------------------|-------------------------|----------------------|
| 500 | 1002 | 97.1 | 5.6 |
| 600 | 566 | 98.3 | 10.5 |
| 700 | 411 | 98.8 | 15.3 |
| 800 | 344 | 99.0 | 19.9 |
| 900 | 317 | 99.1 | 22.9 |
| 1000 | 304 | 99.1 | 26.2 |

FIGURE II-1

Performance of Modified MSI-400 Membrane

as a function of Pressure

Feedwater - 34,200 p/m NaCl - 75°F



B. MODIFIED SMALL-SCALE MSI-400 OPTIMIZATION

1. Objective

The first objective of this contract was to improve flux and rejection in laboratory frames of the membrane barrier layer MSI-400 for seawater conditions by altering the concentration of reaction components. As stated previously, the performance goal was 20 GFD and 99.5% rejection at 800 psig on a feedwater containing 35000 mg/l NaCl. To achieve this, the work was divided into four phases as follows:

Phase I - Primary PEI Concentration Study

Phase II - IPC Concentration Study

Phase III - Secondary PEI Concentration Study

Phase IV - Acid Acceptor Study

2. Phase I - Primary PEI Concentration Study

At the beginning of all MSI-400 modification work, a standard procedure for making the membrane was chosen, based on previous experience with the brackish water membrane. The polysulfone porous support material is supported between two teflon frames clamped together. The membrane is then made according to the procedure in Table II-2.

As stated previously, preliminary optimization work held the PEI concentration constant at 2.3% and varied the IPC concentration. Under high pressure testing on seawater feed, a membrane made with 0.6% IPC in Shell 335 DC solvent demonstrated the best flux and rejection characteristics. Consequently, this value was chosen to be held constant during the Phase I work.

TABLE II-2

STANDARD FRAME PROCEDURE FOR FORMATION OF MODIFIED
MSI-400 MEMBRANE

- (1) Deionized water rinse
- (2) Aqueous PEI residence _____ 4 min.
- (3) Drain period, frame vertically
suspended _____ 0.5 min.
- (4) Organic IPC reaction period _____ 1.5 min.
- (5) Rapid vertical drain
- (6) Horizontal evaporation period _____ 5 min.
- (7) Heat treatment _____ 15 min.
(in circulating air oven or
beneath infrared lamp)*

*Discussed later

Aqueous PEI solutions at 1.5, 2.0, 2.3, 2.5, 3.0, 3.5, 4.0 and 5.0% concentrations were used to make MSI-400 membranes with 0.6% IPC. Each contained a small amount of Sodium Dodecylsulfate (SDS) which is used to insure uniform wetting of the polysulfone. This range was established as a logical starting point, as it provided data from PEI concentrations both higher and lower than the standard optimized brackish water value of 2.3%. All solutions were made with a 0.3% concentration of the acid acceptor, tribasic sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$). This component is also a standard in the formation of the brackish membrane and the concentration value is a result of previous work. Under the current contract, an acid acceptor analysis was performed and is detailed in Phase IV.

As indicated in Table II-2, the membrane formation procedure has two alternative methods of heat treating the membrane in the final stage of formation, namely in a circulating air oven or beneath an infrared lamp. Because it was not clear which of the two would be most conducive to good performance characteristics, this was also studied during the primary PEI concentration study. Two sets of membranes were made in the above 1.5 to 5.0% range, identical in all respects other than the heat treatment method. The summarized results after testing all the membranes on seawater feed at 800 psig are shown in Table II-3 and Figure II-2.

TABLE II-3

PRIMARY PEI CONCENTRATION STUDY MSI-400 MEMBRANE
CHARACTERISTICS AT 0.6% IPC AND VARIABLE PEI CONCENTRATION
SEAWATER 35000 ppm NaCl FEED
800 PSIG

| <u>PEI CONCENTRATION</u> | <u>FLUX, GFD</u> | | | <u>% REJECTION</u> | | |
|--------------------------|------------------|-----------|-----------------------------|--------------------|-----------|-----------------------------|
| | <u>OVEN</u> | <u>IR</u> | <u>\bar{X}</u> | <u>OVEN</u> | <u>IR</u> | <u>\bar{X}</u> |
| 1.5% | 16.2 | 24.0 | 20.1 | 97.5 | 91.9 | 94.7 |
| 2.0 | 20.5 | 18.3 | 19.4 | 98.4 | 98.5 | 98.5 |
| 2.3 | 12.8 | 13.8 | 13.3 | 98.4 | 98.7 | 98.6 |
| 2.5 | 15.0 | 16.2 | 15.6 | 98.3 | 98.6 | 98.5 |
| 3.0 | 16.5 | 17.7 | 17.1 | 98.9 | 98.7 | 98.8 |
| 3.5 | 10.6 | 13.5 | 12.1 | 98.8 | 98.0 | 98.4 |
| 4.0 | 12.2 | 19.7 | 16.0 | 98.2 | 98.1 | 98.2 |
| 5.0 | 20.2 | 26.2 | 23.2 | 97.7 | 93.8 | 95.8 |

PRIMARY PEI CONCENTRATION STUDY

MSI-400 MEMBRANE

35000 mg/l NaCl/ 800 PSIG

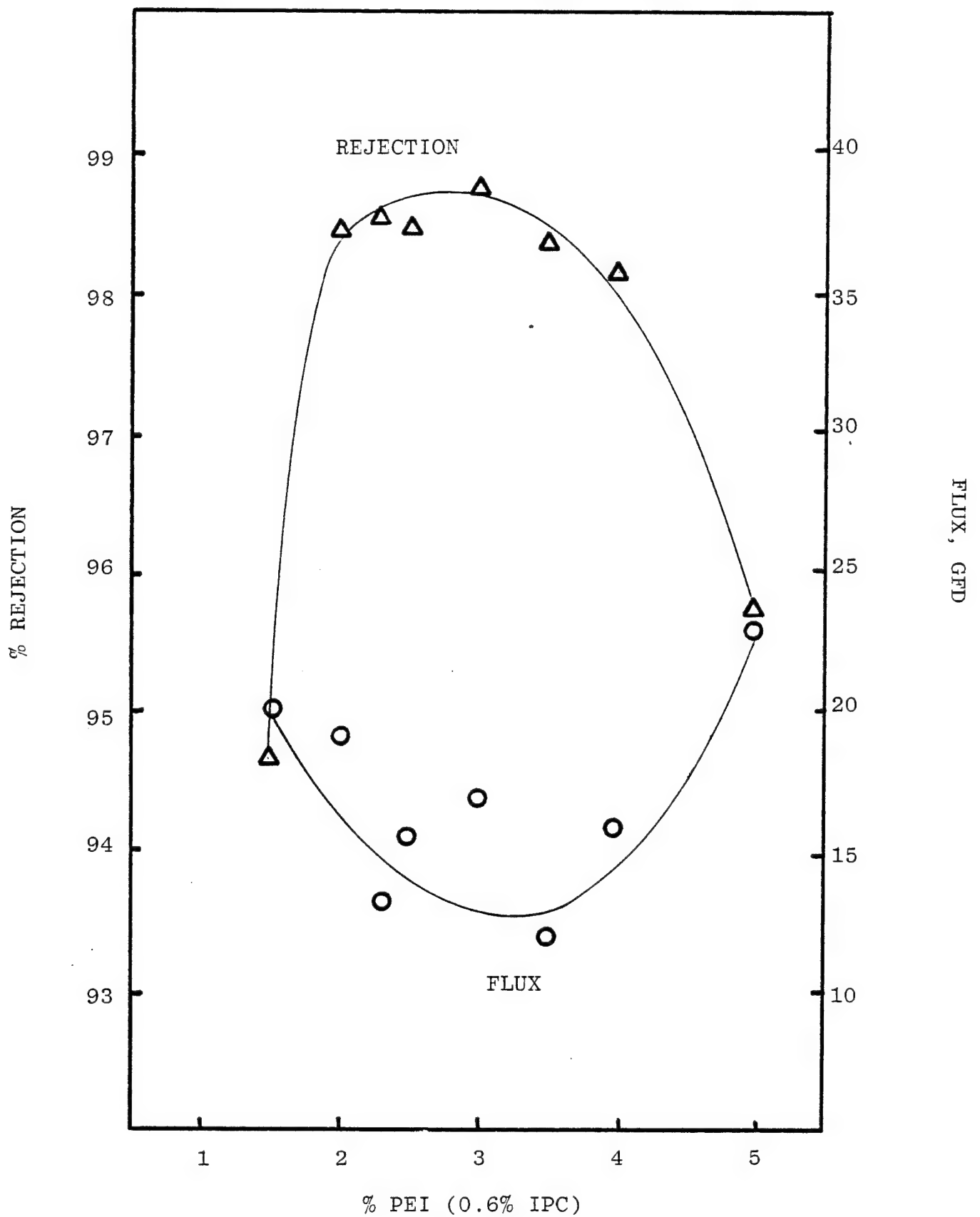


FIGURE II-2

Analysis of the data presented indicated that the optimal trade-off between flux and rejection membrane characteristics occurred with a PEI concentration value of 2.5%. The data also suggested that infrared curing gives a slight improvement over heat treatment in a circulating air oven.

3. Phase II - IPC Concentration Study

The work reported above indicated that for a concentration of 0.6% IPC, a value of 2.5% PEI would generate a membrane with optimal flux and rejection qualities. This conclusion however, was merely preliminary and Phase II work began. Using the 2.5% PEI concentration, a series of experiments was conducted to determine whether 0.6% truly is the optimal IPC concentration at that specific PEI value. Thus, membranes were made holding PEI at 2.5% with a 0.3% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ concentration and varying the IPC concentration. Consequently, membranes were made on polysulfone porous support according to the standard membrane formation procedure with the IPC concentration varying from 0.2% to 2.4%. This constituted a wide range of IPC concentration from a very small IPC/PEI ratio to one essentially at unity. Additionally, membrane formation included infrared curing of all samples based on the results of Phase I work.

It must be noted that the formation of membranes is a very complex process and in spite of a standard procedure, it is often extremely difficult to reproduce membrane results. The large number of variables involved require careful technique and as large a data pool as possible. Consequently,

much of the time devoted to reactant concentration analysis must of necessity be devoted to work that endeavors to repeat membrane results.

The data resulting from the Phase II IPC Concentration Study is shown in Table II-4 and Figure II-3. Again, all membranes were tested on a seawater feed of 35,000 mg/l NaCl at 800 psi applied pressure with the data normalized to 75°F. Seven different series of membranes were made and the mean of all values is presented.

From the membranes made and tested, it appeared that an IPC concentration of 1.2% at 2.5% PEI generated a membrane with the highest salt rejection and adequate water flux. As the IPC concentration increases, it is apparent that the flux decreases linearly. This is thought to be due to a thicker membrane barrier probably being formed. Alternatively, the rejection has a value at which it peaks.

4. Phase III- Repeat PEI Concentration Study

In the repeat PEI concentration work, the IPC concentration was held constant at 1.2% IPC, while the PEI concentration was once again varied as in Phase I. Membranes were made on polysulfone according to the standard procedure with 1.5, 2.0, 2.5, 3.0 and 3.5% PEI solutions.

Initial experience during this phase of work indicated a slight scorching on the surface of the membrane when exposed to heat treatment for fifteen minutes under the infrared light.

TABLE II-4

IPC CONCENTRATION STUDY MSI-400 MEMBRANE
CHARACTERISTICS AT 2.5% PEI AND VARIABLE IPC CONCENTRATION
SEAWATER 3500 mg/l NaCl FEED
800 PSIG
IR HEAT CURED

| <u>IPC CONCENTRATION</u> | <u>FLUX, GFD</u> | <u>% REJECTION</u> |
|--------------------------|------------------|--------------------|
| 0.2% | 20.0 | 93.0 |
| 0.4 | 14.3 | 96.0 |
| 0.6 | 13.9 | 96.3 |
| 0.8 | 13.8 | 96.7 |
| 1.0 | 13.2 | 96.7 |
| 1.2 | 11.7 | 97.4 |
| 1.6 | 11.8 | 96.3 |
| 2.4 | 8.6 | 97.2 |

IPC CONCENTRATION STUDY
MSI-400 MEMBRANE
35000 mg/l NaCl/ 800 PSIG

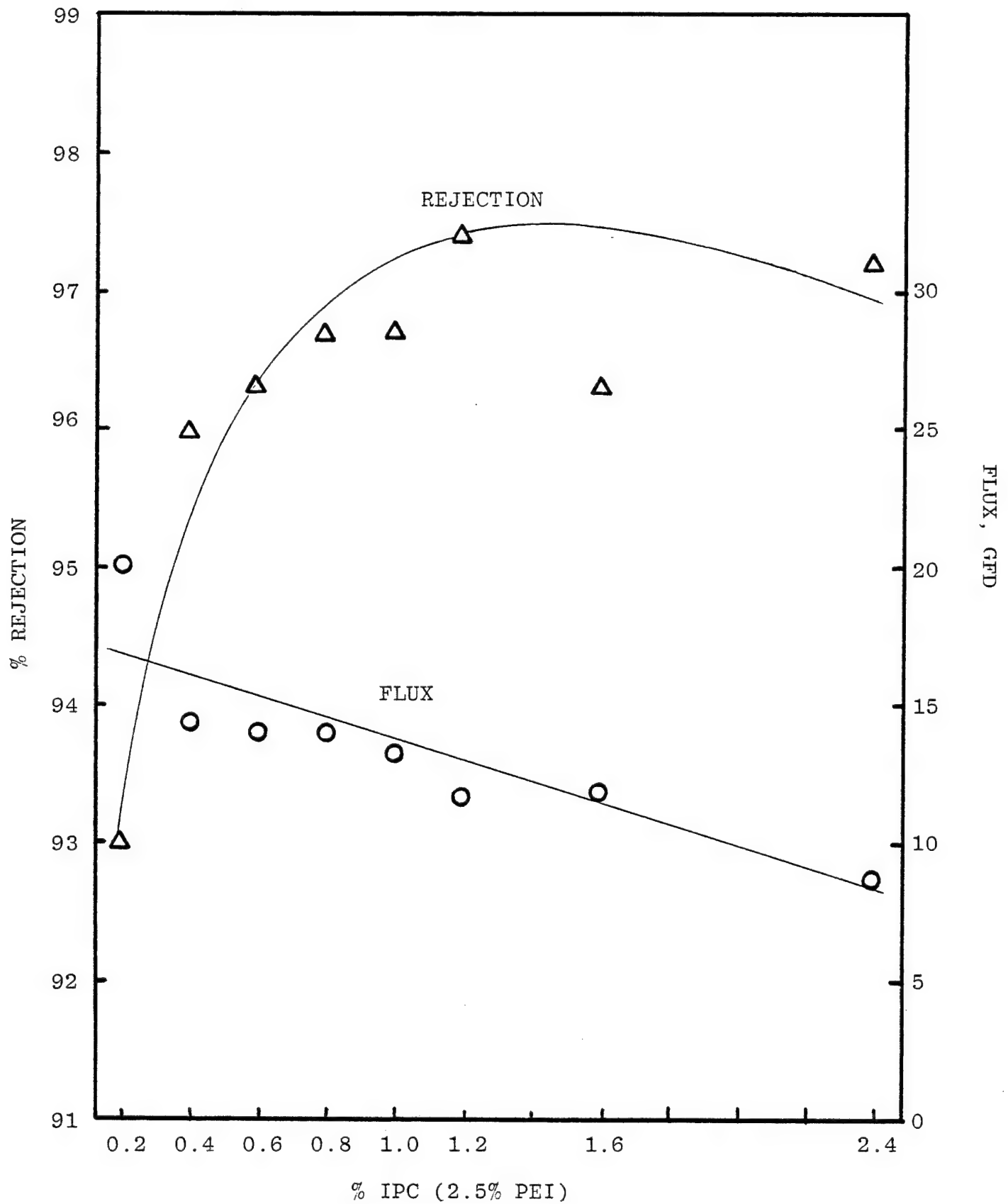


FIGURE II-3

This had not occurred previously and no change had been made in the heating technique to explain the phenomena. Although Phase I work indicated that infrared curing gives slightly improved membrane characteristics over oven curing, it was decided that due to the scorching problem, a change to the oven method would be necessary.

Five series of membranes were made with 1.2% IPC and varying the PEI concentration. The summarized data is in Table II-5 and Figure II-4. All samples were tested on a seawater feed of 35,000 mg/l NaCl at 800 psig. Inspection of the tabulated data indicates that a PEI concentration of 2.0% and an IPC concentration of 1.2% generates a membrane with higher flux and rejection than the previous standard 2.5% PEI.

At this stage of work, the analysis of PEI and IPC concentration was halted. The technique of holding one reactant concentration constant while varying the other, determining its optimum value, and then repeating the process with the new information for the first reactant has generated important results. Although it could have been continued, limitations imposed by time and the fact that major improvement in the modified seawater MSI-400 membrane had been accomplished, the concentration studies were concluded.

5. Phase IV - Acid Acceptor Study

As previously mentioned, in the context of work accomplished with the Self Directing Optimization performed on the brackish

TABLE II-5

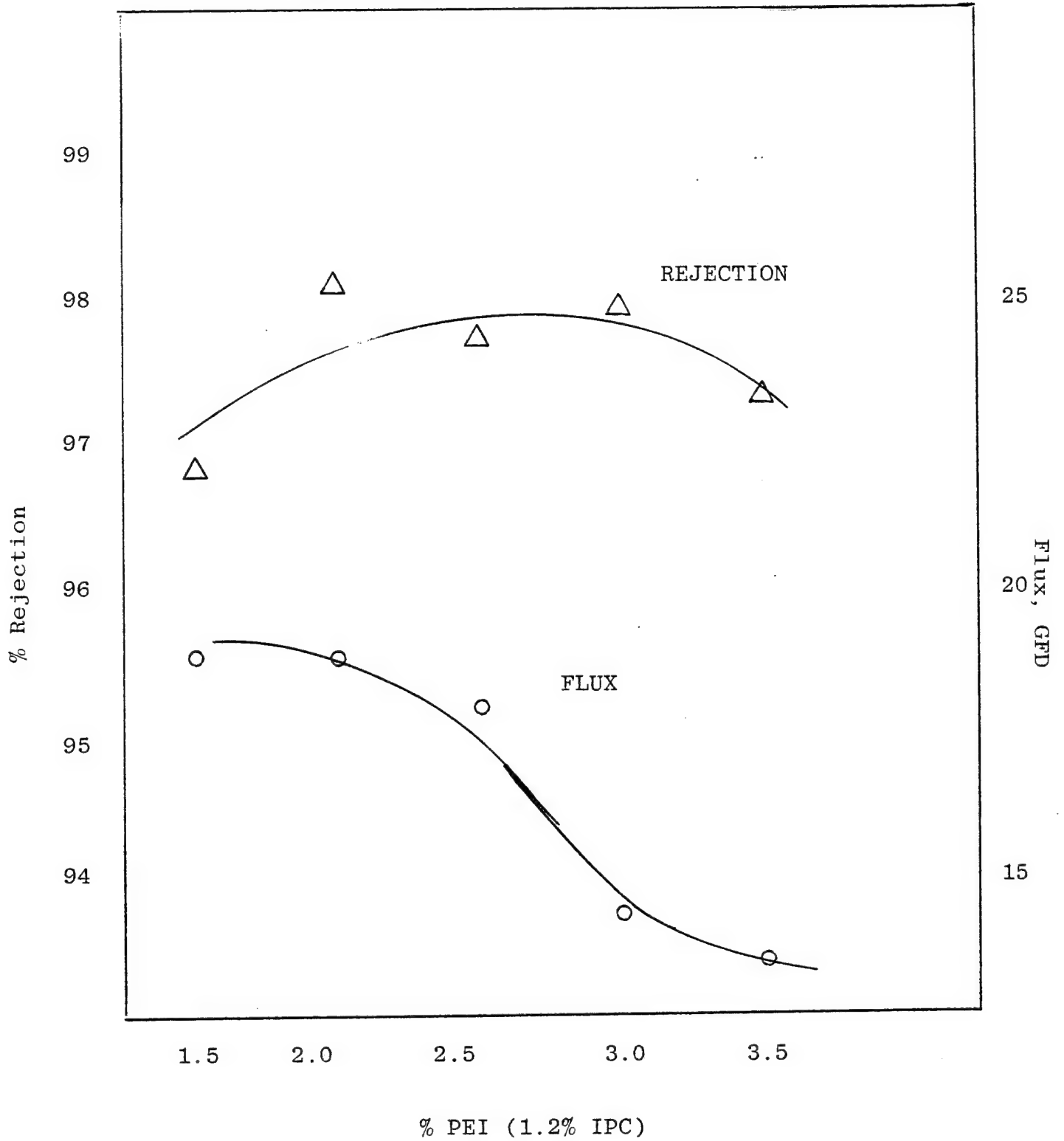
REPEAT PEI CONCENTRATION STUDY MSI-400 MEMBRANE
CHARACTERISTICS AT 1.2% IPC AND VARIABLE PEI CONCENTRATION
SEAWATER 35,000 mg/l NaCl FEED
800 PSIG
OVEN HEAT CURED

| <u>PEI CONCENTRATION</u> | <u>FLUX, GFD</u> | <u>% REJECTION</u> |
|--------------------------|------------------|--------------------|
| 1.5% | 18.7 | 97.3 |
| 2.0 | 18.7 | 97.9 |
| 2.5 | 17.9 | 97.7 |
| 3.0 | 14.2 | 98.1 |
| 3.5 | 13.4 | 96.8 |

FIGURE II-4

Repeat PEI Concentration Study MSI-400 Membrane

35,000 mg/l NaCl/800 psig



water MSI-400, an acid acceptor is a secondary component in the interfacial reaction mixture. Previous work indicated that 0.3% tribasic sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) is important in membrane barrier formation although is of secondary importance in comparison with reactant concentrations. Study to determine the effect of an acid acceptor on the modified MSI-400 for seawater was divided into two parts: (1) a survey of various acid acceptors at a concentration of 0.3% and (2) an examination of various concentrations of the acid acceptor determined superior in (1).

For the initial work, several readily available acid acceptor candidates were chosen. Using the standard barrier formation procedure, membranes were made with (1) sodium phosphate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, (2) potassium hydroxide, KOH, (3) sodium hydroxide, NaOH, (4) ammonium hydroxide, NH_4OH and (5) no acid acceptor. All membranes were made with 1.2% IPC and 2.0% PEI on polysulfone porous support and heat treated in a circulating air oven. The averaged results of three series of membranes when tested on seawater feed, are shown in Table II-6.

The membranes made with 0.3% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and with no acid acceptor clearly gave the most favorable flux and rejection properties. Visual inspection of the samples, upon completion of the testing, showed that the tabulated results correlated with the visible condition of the membrane. The seawater feed has methylene blue dye in it, and membranes

TABLE II-6

ACID ACCEPTOR SURVEY MSI-400 MEMBRANE CHARACTERISTICS AT
1.2% IPC AND 2.0% PEI
800 PSIG
OVEN HEAT CURED

| <u>ACID ACCEPTOR (0.3% CONCENTRATION)</u> | <u>FLUX, GFD</u> | <u>% REJECTION</u> |
|---|------------------|--------------------|
| $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ | 26.1 | 97.6 |
| KOH | 43.6 | 43.8 |
| NaOH | 49.1 | 29.9 |
| NH_4OH | 8.8 | 96.1 |
| No acceptor | 24.6 | 97.7 |

retain dye in areas of imperfection. Those samples which demonstrated poor rejection and low flux consistently showed major dye uptake.

To study the effects on membrane performance of varying the sodium phosphate concentration, membranes were made at 0, 0.1, 0.2, 0.3, 0.8, 1.0, and 3.0% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ under the same standard conditions for the acid acceptor survey work. The results of this are in Table II-7 and Figure II-5. Analysis of the data shows that the optimal MSI-400 membrane is produced with 0.1% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ as the acid acceptor in the interfacial reaction mixture.

At the conclusion of the above work, two membranes were made incorporating the results obtained in all phases of the modified small-scale MSI-400 for seawater. Made on polysulfone support according to the standard procedure with 1.2% IPC, the mean of 12 samples demonstrated a flux of 16.2 GFD and 99.3% rejection with some single samples having rejections as high as 99.5%. This represents a significant step forward in the state of seawater desalination capabilities with this membrane.

TABLE II-7

MSI-400 CHARACTERISTICS AS A FUNCTION OF $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$

CONCENTRATION

SEAWATER 3500 mg/l NaCl FEED

800 PSIG

OVEN HEAT CURED

1.2% IPC/2.0% PEI

| <u>$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ CONCENTRATION</u> | <u>FLUX, GFD</u> | <u>% REJECTION</u> |
|---|------------------|--------------------|
| 0% | 22.3 | 98.1 |
| 0.1 | 18.7 | 99.0 |
| 0.2 | 23.5 | 98.4 |
| 0.3 | 24.4 | 98.7 |
| 0.8 | 39.3 | 86.0 |
| 1.0 | 61.8 | 67.0 |
| 3.0 | 68.4 | 30.9 |

MSI-400 Characteristics as a Function of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ Concentration
1.2% IPC/20% PEI

Flux, GFD

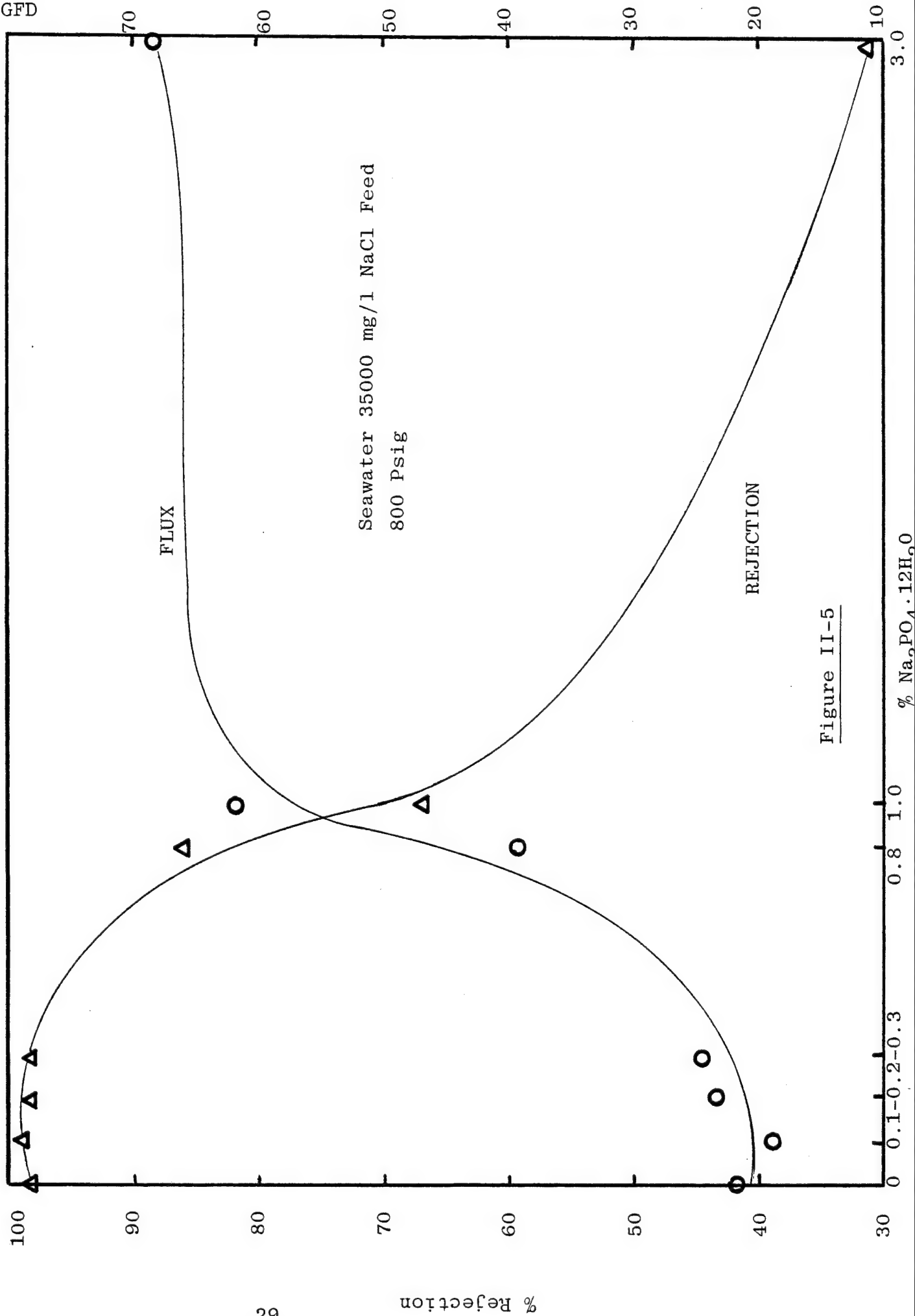


Figure II-5

% $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$

C. CONTINUOUS CASTING

1. Polysulfone Support Castings

During the laboratory development and at the beginning of the two inch module fabrication period, porous support preparations had utilized Eaton-Dikeman 3361 fabric carrier material. A formulation of 17% polysulfone/17% methyl cello-solve/66% dimethylformamide with a casting speed of 28 feet/min were used. It was apparent that porous support made with this material had three disadvantages compared to support made with the Pellon 6100 material. First, variable porosity of Eaton-Dikeman 3361 allowed the casting solution to bleed through and this ultimately lead to pinholes in the finished support. Second, this well-calendered material has a smooth surface which does not allow adequate glue adhesion in module fabrication without modification of the surface to be glued. Lastly, it is apparent from the observation of o-ring damage to membrane in test cell samples that the applied membrane has a more delicate nature than that applied on Pellon 6100 porous support. For these reasons, all polysulfone porous support preparations during the continuous casting studies were fabricated with Pellon 6100 fabric carrier material. A formulation of 16.3% polysulfone/6.2% methyl cellosolve/1.8% bis(2-methoxyethyl) ether/75.7% dimethylformamide and a casting speed of 20 ft/min were used for fabrication of porous supports during the continuous casting phase.

2. Continuous Interfacial Applicator (IFA) Prepared Membrane

Studies have been conducted with the continuous interfacial applicator, which is schematically shown in Figure II-6, in order to optimize the desalination properties of MSI-400 membrane for low pressure membrane. It was decided to carry out these studies with the continuous IFA since this machine is capable of efficiently producing the quantities of consistently high quality membrane necessary for two inch seawater modules.

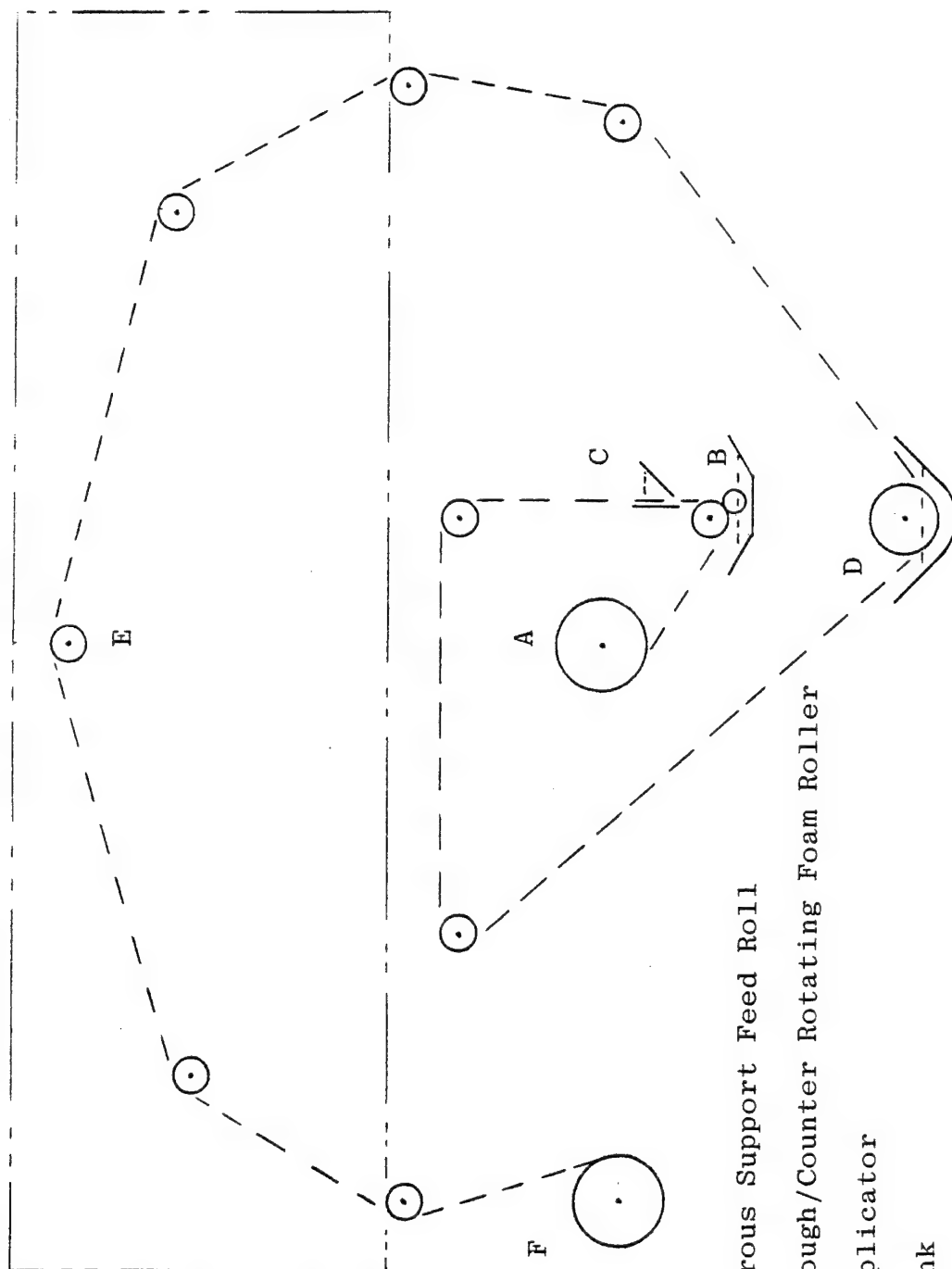
Section II-B of this report describes the optimization of solution (aqueous and organic) formulations for preparation of seawater desalination membranes on a laboratory scale. This phase demonstrated the art of the possible and pointed to relationships of membrane formation variable. However, when membrane barrier layer formation is attempted on a continuous machine, it is necessary to optimize the variables for that particular machine. This is due to changes in such conditions as air dry time, reaction time, heat cure time, etc.

3. PEI Concentration Study

Optimization of the PEI concentration in the aqueous phase was the first variable studied. This experiment was carried out holding IPC concentration constant at 1.8% and varying the PEI concentration from 3.0 to 6.0%.

Results of the PEI concentration study shown in Table II-8 suggest that improved salt rejection of IFA prepared MSI-400 membrane could be obtained using the higher PEI concentrations.

FIGURE II-6



- A - Wet Porous Support Feed Roll
- B - PEI Trough/Counter Rotating Foam Roller
- C - PEI Applicator
- D - IPC Tank
- E - Hot Air Oven
- F - Membrane Take-up Roll

TABLE II-8

PEI CONCENTRATION STUDY WITH 1.8% IPC - IFA PREPARED MEMBRANE

| <u>% PEI</u> | <u>Samples Tested</u> | <u>Flux, GFD</u> | <u>Rejection %</u> |
|--------------|---------------------------|----------------------|------------------------|
| 6.0 | 3 | 11.9 | 97.5 |
| 5.8 | 6 | 16.4 | 98.3 |
| 5.5 | 3 | 19.2 | 95.8 |
| 3.0 | 3 | 24.3 | 95.2 |

Test conditions: 800 psig, 34,300 mg/l NaCl, pH 5.5

A modification of the PEI application method was made for this study by replacing the stationary foam aqueous applicator (which had been used exclusively in the past), with a counter rotating foam aqueous applicator. It was felt that this cylindrical applicator, which is rotated in the PEI solution, would combine an effective cleansing step with the PEI application. It was found, however, that the counter rotating wick allowed foam from the PEI trough to be carried well past the application area. This resulted in bubbles being carried as far as the IPC trough, whereupon irregular membrane appeared to form. For comparison, a previous study with 5.8% PEI and 1.8% IPC using the stationary wick is listed in Table II-9.

TABLE II-9

IPC CONCENTRATION STUDY WITH 5.8% PEI - IFA PREPARED MEMBRANE

| <u>% IPC</u> | <u>Samples Tested</u> | <u>Flux, GFD</u> | <u>Rejection %</u> |
|--------------|---------------------------|----------------------|------------------------|
| 2.7 | 5 | 14.5 | 98.9 |
| 2.3 | 4 | 12.0 | 98.3 |
| 1.8 | 6 | 18.1 | 98.3 |
| 1.4 | 6 | 21.5 | 97.6 |

Test conditions: 800 psig, 34,300 mg/l NaCl, pH 5.5

4. PEI Application Method Study

A series of experiments (using 5.8% PEI and 1.8% IPC) that were designed to improve the PEI application step of IFA prepared MSI-400 membrane were begun with various application methods. These consisted of counter rotating, freely rotating and non-rotating modes of the roller applicatores as well as dipping only and stationary foam application methods.

Of the seven methods evaluated, the two which showed best results were the stationary applicator and the counter rotating mode of the roller application, producing membranes with 15.4 gfd flux and 97.3% rejection (mean of 10 samples and 17.6 gfd flux and 97.4% rejection (mean of 6 samples) respectively.

From this point on, all future IFA prepared membranes were made using a combination of the above described best methods. The counter rotating applicator not only applies the aqueous solution, but cleanses the membrane prior to the the final application by the stationary applicator.

5. PEI Wick Material Study

It was evident that very fine scratches have been produced on the porous support after the application of PEI solution. Since these scratches have been correlated to poor membrane performance, a study was made on different types of foam materials for the stationary applicator. Six applicator materials were tested and each of these were fabricated from a relatively soft ether-type polyurethane foam. The PEI and IPC concentrations used were 5.8% and 1.8%, respectively.

The resultant membranes exhibited fluxes ranging from 14.3 to 19.4 gfd and rejections from 97.6% and 98.6% at 800 psi on a feedwater with about 35,000 mg/l NaCl at 800 psig at 75°F. The best material was a Keystone 1114F foam, producing 17.3 gfd flux with 98.6% rejection. Qualities which the best stationary applicators have in common are a foam with a relatively large pore size and a somewhat closed cell structure.

6. IPC Concentration Studies

In efforts to further optimize IFA prepared MSI-400 seawater membrane, two additional experiments were carried out by varying the IPC concentration and retaining PEI at a fixed concentration.

The first experiment held PEI concentration constant at 5.8% while varying the IPC concentration from 2.7% to 1.4%. Results are shown in Table II-9 and these results indicate that salt rejection improved with increasing IPC concentration.

However, the flux approached rather low values. It should also be mentioned that every IPC concentration tested produced membrane with a slightly adhesive finish. It is possible that these higher concentrations of PEI (i.e., 5.8%) create a thicker layer which is more difficult to heat cure.

It was believed that a study similar to that above, conducted with 3.5% PEI, would overcome the disadvantages of difficult heat curing and low flux. This concentration of PEI was used with varying IPC concentrations of 0.4% to 3.0%. Better desalination properties did in fact result, while maintaining relatively high fluxes as revealed in Table II-10 and in Figure II-7.

A review of data in Table II-10 and Figure II-7 also shows that the flux decreases as a function of increasing IPC concentration and the rejection increases with increasing IPC concentration. Both of these tend to approach asymptotic values which are 99% for the rejection and about 17 GFD for flux. Subsequent membrane fabrications on the IFA using an IPC concentration of 2.3% and a PEI concentration of 3.5% repeatedly yielded MSI-400 seawater type membrane with mean values (9 samples) of 99% rejection and a flux of 17 GFD.

TABLE II-10

IFA PREPARED MSI-400 MEMBRANE - IPC CONCENTRATION STUDY WITH 3.5% PEI

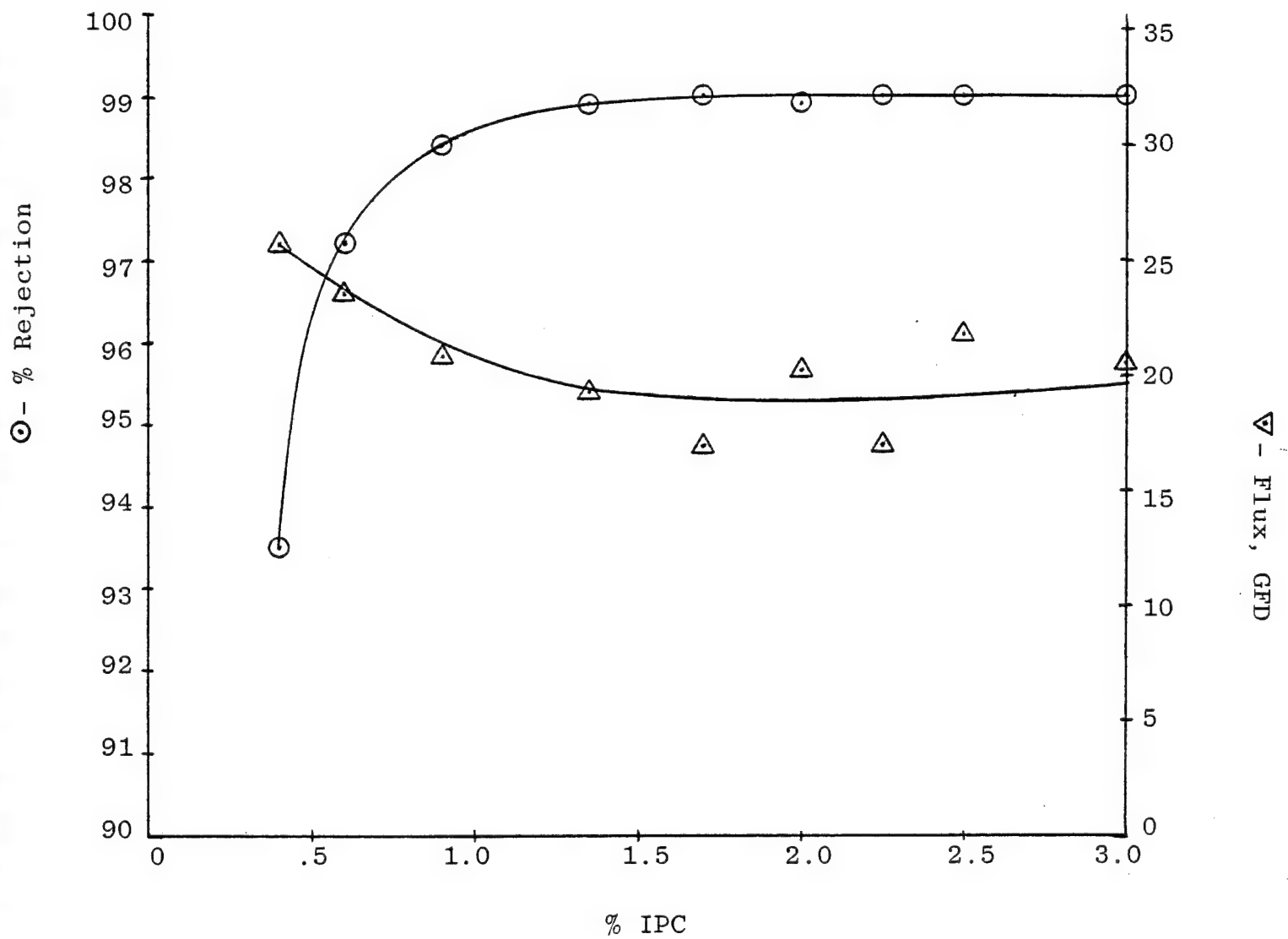
| <u>% IPC</u> | <u>Samples Tested</u> | <u>Flux, GFD</u> | <u>Rejection %</u> |
|--------------|---------------------------|----------------------|------------------------|
| .4 | 6 | 25.7 | 93.5 |
| .6 | 6 | 23.2 | 97.2 |
| .9 | 6 | 20.8 | 98.4 |
| 1.4 | 10 | 19.3 | 98.9 |
| 1.7 | 6 | 17.0 | 99.0 |
| 2.0 | 10 | 20.2 | 98.9 |
| 2.3 | 9 | 17.1 | 99.0 |
| 2.5 | 5 | 21.8 | 99.0 |
| 3.0 | 3 | 20.6 | 99.0 |

Test conditions: 800 psig, 34,300 mg/l, pH 5.5

FIGURE II-7

IFA Prepared MSI-400 membrane

IPC Concentration Study with 3.5% PEI



Test Conditions: 800 psi seawater (34,300 ppm NaCl)
pH approximately 5.5

Experimental Conditions

The conditions given here were employed when producing MSI-400 seawater membrane on the continuous IFA. These conditions applied to membranes prepared during the IPC studies and all those produced thereafter. Machine speed was 2 ft/min, with an air oven temperature of approximately 115°C. The PEI solution contained 0.1% tribasic sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) acid acceptor and 0.02% sodium dodecyl sulfate wetting agent. This solution was applied by the counter rotating-stationary wick combination described earlier.

MSI-400 membrane performance was evaluated on a feed-water containing 34,300 ppm NaCl at pH 5.5 ± 0.3 and 800 psig.

D. SPIRAL WOUND ELEMENT FABRICATION

1. Background

Spiral wound element fabrication techniques have been developed under OSW and OWRT contracts. Consequently, it was anticipated that the major problem would be the preparation of membrane of sufficient quality for incorporation into the module configuration.

The completed element has dimensions 1-7/8 inches in diameter and 11-1/8 inches in length. The element is of single leaf construction with a leaf length of 33 inches. The major components of the element are as follows:

1. (MSI-400 Seawater) membrane barrier layer on polysulfone porous support.
2. Product water carrier material - Simplex.
3. Brine spacer - Dupont 15 PDS Vexar.
4. Adhesive - Hexcel 6108 polyurethane (unless otherwise noted).
5. PVC product water tube with two opposing rows of 1/16" diameter holes spaced every 3/4 inch.
6. Outer wrap - 3M #471 white vinyl tape.
7. Brine seal - 1/4 inch x 1/4 inch polyurethane foam wrapped with 4 mil Teflon tape.

The elements fabricated early in this program were produced from MSI-400 membrane made on the batch IFA. Casting formulations for the batch IFA originally were 2.0% PEI containing 0.3% acid acceptor with the same wetting agent concentrations as for the continuous IFA and IPC concentration was 1.2%.

Problems of discontinuous (low salt rejection) membrane prompted an increase in PEI concentration to 5.0%. The increase proved to successfully solve this problem and thus the later batch IFA productions utilized 5.0% PEI with 1.2% IPC.

Later in the program, conditions were optimized for the production of membrane on the more efficient continuous IFA. The majority of the two inch elements were fabricated with membrane produced from this IFA under optimal conditions previously mentions.

Testing of the two inch element was done at 800 psig for 1 hour on a feedwater containing about 34,3000 mg/l NaCl at a pH of 5.5 and 75⁰F. Elements which exhibited low salt rejection under these conditions were then subjected to a dye test. The defective elements were tested in a pressure vessel containing an aqueous solution of methyl violet dye at 220 psi. Careful observation of dye uptake in the dismantled module yielded specific information as the sources of failure.

2. Module Production

As a result of extensive dye test analyses, five major sources of module failure were observed. These sources were catagorized as follows:

- Fabric carrier material: protruding fibers, creases, variable density leading to pinholes in porous support.
- Membrane: discontinuities from its formation, degradation under test.
- Fabrication: technique errors.

Adhesion: to product water tube, to fabric carrier material.

Testing: telescoping caused by pulsating pressure or excessive brine flow rate.

These five sources are discussed throughout the element development program and are summarized in Table II-11.

Due to the large number of modules fabricated, a summary composed of five phases of development is given below.

a. Phase I

This early period of module development utilized batch IFA membrane (2.0% PEI). Testing produced salt rejection in the low 90% range.

All but one of the seven modules failed due to discontinuous membrane. The remaining one failed due to lack of adhesion. Eaton-Dikeman 3361 fabric carrier material (sanded at glue areas to improve adhesion) and Uralite 6108 adhesive were used throughout this phase.

b. Phase II

Batch IFA membrane prepared with the modified PEI concentration (5.0%) was incorporated into this phase of element development. All six of these elements utilized Eaton-Dikeman 3361 fabric carrier material.

The first two elements were fabricated with a lower viscosity polyurethane adhesive, P.C. 6455, in an attempt to eliminate the sanding step required when using Eaton-Dikeman 3361. This proved to be inadequate since both of these elements failed due to poor adhesion. Salt rejections were in the 94% range.

The next series of four elements (prepared with Uralite 6108) were fabricated in order to test the effectiveness of a protective coating of polyvinylalcohol (PVA) on the membrane surface and of heat sealing near the glue lines of the membrane. There were indications that leakage had occurred between the Eaton-Dikeman 3361 material and the polysulfone porous support. By heat sealing, the two materials are fused together making leakage by separation virtually impossible. The best combination proved to be both PVA treatment and heat sealing. The one element which had both of these treatments exhibited 10.5 gfd flux and 97.9% rejection on seawater. The remaining three elements produced rejections of about 96% and showed signs of damage caused by strongly pulsating conditions during testing.

c. Phase III

Continuous IFA membrane was incorporated into all but one of the nineteen elements completed during this period. Ten of these elements were prepared with Texlon 715 backing and nine with Pellon 6100. P.C. 6455 adhesive was used in four elements and Uralite 6108 in the remainder.

Four elements produced fluxes of 14.5 to 20.2 gfd and rejections of 97.0 and 97.5%. These were all prepared from Texlon 715 and Uralite 6108 adhesive. It was found that adhesion was improved by fabricating fewer elements per batch of adhesive at one time. In this way, viscosity was kept low and better glue penetration was obtained.

The remaining fifteen elements provided rejections in the 96% range. The two causes of failure were defects associated with the fabric carrier material and problems in the fabrication technique.

d. Phase V

This period saw the production of seven elements using the three different fabric carrier materials. A new adhesive, FP 1211, was tried in six of these elements since it was shown to have better adhesion than Uralite 6108 in membrane/Simplex test samples. The remaining element was made with P.C. 6455 adhesive, which was also shown to have improved adhesion in test samples. It was expected that FP 1211 would provide better sealing of the holes in the membrane caused by the fabric carrier material. Though overall adhesion to the backing material compared favorably to Uralite 6108, adhesion to the PVC product water tube appeared to be worse. The same behavior was observed when using P.C. 6455. As a result, all but one of the seven elements yielded very low rejections - attributed to poor adhesion of the Simplex to the product water tube. The best element provided a flux of 15.9 gfd and rejection of 97.3%. Texlon 715 backing and FP 1211 adhesive were used in this element.

e. Phase V

The final phase of element development incorporated the knowledge gained from previous successes as well as failures. Discussed below are the various choices made for materials and techniques in this last phase of element fabrication.

1) Pellon 6100 Backing Material: Pellon 6100 - (poly-sulfone porous support) has produced the highest, most consistent quality IFA membrane of the three backing materials tested. It was believed that the fiber problem of Pellon 6100, though a serious one, was less serious than the problems associated with eight Eaton-Dikeman 3361 or Texlon 715.

2) Membrane Pretreatment: Polyvinylalcohol (PVA-2,000 M.W., 5% aqueous) solution cured on the membrane surface has demonstrated some protection against the abuse during module rolling. In addition, heat sealing of the glue-line areas was included as a safeguard against brine intrusion through the polysulfone/Pellon 6100 interface.

3) PVC Product Water Tube Pretreatment: These were thoroughly cleaned with methyl ethyl ketone solvent, then sanded at the gluing surfaces to promote maximum adhesion. Also in the past, it was found that when spraying the entire PVC tube length with 3M-77 adhesive, product tube leaks resulted. It is believed that this spray adhesive (used to tack the Simplex in place) interfered with the primary adhesive (i.e., Uralite 6108, etc.). For this reason, only the center of the product tubes were sprayed, leaving the primary gluing surfaces of the product water tube more receptive to main adhesive.

4) Additional Fabrication Techniques: The Simplex product spacer, a rather stiff material, has demonstrated problems in adhering to the product water tube. By using a four inch long Pellon 6800 leader attached to the Simplex, better adhesion was obtained.

The other addition has been the technique of double gluing. To provide increased glue contact and thus better adhesion, glue was applied to both Simplex and membrane backside during the rolling procedure.

5) Uralite 6108 Adhesive: This adhesive appeared to be more effective against product tube leakage than others tested. When mixed such that air entrainment did not occur, and when used quickly, very good adhesion in the element was observed.

A much improved success rate was seen in this last phase of element production. Eight elements, out of nineteen total, had fluxes ranging from 12.8 to 18.3 gfd and rejection ranging from 97.0 to 97.9%. The remainder provided rejections in the 95% range.

Failure was attributed primarily to fabric carrier material related defects which were not successfully repaired.

Table II-11 shows the prevalence of element failure attributed to each of the five major areas. It can be seen that in the early stages, element failed primarily due to poor membrane. This problem was largely overcome by utilization of the continuous IFA membrane. Difficulties in adhesion and

fabrication technique experienced in the middle of the program, were minimized during phase V. As improvements in other areas were made, the limiting factor to superior element performance narrowed to defects in the fabric carrier material.

As discussed previously, defects found in all three of the fabric carrier materials tested, produce large holes in the polysulfone porous support and ultimately lead to holes in the membrane barrier layer. These holes, though often clearly visible, were very difficult to patch effectively. Many different adhesives and techniques were tried, but were met with limited effectiveness. It is believed that substantial improvements in module performance is not possible until refinements in fabric carrier materials are made.

TABLE II-11

Prevalence of Element Failures in each of the Five Major Areas

| <u>Phase of Development</u> | <u>Fabric Carrier Material</u> | <u>Membrane</u> | <u>Fabrication</u> | <u>Adhesion</u> | <u>Testing</u> |
|-----------------------------|--------------------------------|-----------------|--------------------|-----------------|----------------|
| I | 2 | 5 | | 1 | |
| II | 2 | 1 | 1 | 2 | 4 |
| III | 8 | | 8 | 4 | 2 |
| IV | 1 | 1 | 1 | 7 | |
| V | 7 | | 4 | 2 | |
| TOTAL | 20 | 7 | 14 | 16 | 6 |

3. Supplemental Polymers

All of the membrane which was incorporated into spiral wound elements contained minor imperfection such as pinholes

which was caused to a large degree by imperfect fabric carrier material. Prior to element fabrication, the membrane leaf was inspected over a light table and the imperfections were marked with a felt pen. Subsequently, these areas were patched by applying glue on the back of the membrane just before the leaf was incorporated into the element. This technique has been effective in the fabrication of low pressure (250 psig) MSI brackish water elements.

Table II-12 shows the initial flux and rejection of 15 elements, i.e., after 1 hour at applied pressure. This table also shows the flux and rejection after a later or interim test at 800 psig for some of the elements. It is noted in every case of subsequent testing, that the interim data showed an increased flux with a decrease in salt rejection. Post-mortem examination of several elements which had been tested at 800 psig with dye in the sump revealed that feedwater was able to pass into the overlying hole and, travel in a tortuous path through the porous support and eventually emerge beyond the perimeter of the glue patch.

Supplemental polymers have been used to enhance the performance of seawater, composite membrane elements. An evaluation of several supplemental polymers under test cell conditions was completed and it was decided to use a recirculating aqueous solution of 0.05% polyvinylmethylether at pH 6 and 200 psig. This solutions was recirculated for 30 minutes and then rinsed with deionized water to remove excess polymer

solution. The supplemental polymer was then fixed by recirculating an aqueous solution of 0.05% tannic acid at pH 4.5 and 200 psig for 30 minutes. Typically, on test cell samples, this process produced an increase in rejection of between 1 to 2% with a decrease in flux of between 15 to 25%.

In Table II-12, it is seen that in most cases, element performance was enhanced by the use of the supplemental polymer. However, the one hour test at 800 psig further deteriorated the patched areas of some of the elements. Furthermore, indications are that application of the supplemental polymer by immersion is not as effective as pressure application.

TABLE II-12

MSI-400 Two-Inch Seawater Module Performance 60 Minute Data
Before and After Supplemental Polymer (S.P.) Addition

| <u>Module</u> | <u>Initial Data</u> | | <u>Interim Data</u> | | <u>Post S.P. Data</u> | |
|---------------|---------------------|------------------------|---------------------|------------------------|-----------------------|------------------------|
| | <u>Flux GFD</u> | <u>Rejection %</u> | <u>Flux GFD</u> | <u>Rejection %</u> | <u>Flux GFD</u> | <u>Rejection %</u> |
| XIX-83-1 | 10.5 | 97.9 | 16.0 | 88.7 | 19.0 | 92.5 |
| -2 | 10.9 | 96.9 | 14.8 | 95.5 | 19.6 | 90.0 |
| -3 | 11.6 | 96.7 | 15.2 | 95.3 | 20.2 | 93.1 |
| -4 | 9.9 | 96.7 | --- | 94.9 | 7.3 | 96.9 |
| XXII-27-1 | 15.0 | 97.5 | --- | --- | 21.3 | 96.2 |
| XXII-38-2 | 15.9 | 97.3 | 22.0 | 95.5 | 16.8 | 96.5 |
| XXI-31-11 | 18.3 | 97.7 | 16.5 | 96.4+ | 17.3 | 97.6 |
| -12 | 15.3 | 97.1 | 10.2 | 96.6+ | --- | --- |
| -13 | 17.5 | 97.9 | | | 15.4 | 98.1 |
| -14 | 17.6 | 97.8 | | | 16.0 | 97.6 |
| -15 | 15.9 | 97.3 | | | 13.6 | 97.6 |
| -16 | 12.8 | 97.0 | 8.1 | 95.7+ | --- | --- |
| -18 | 14.0 | 96.7 | | | 13.0 | 96.9 |
| -19 | 18.0 | 97.0 | 11.7 | 96.6+ | --- | --- |
| -20 | 15.7 | 97.3 | | | 16.6 | 98.3 |

+ Supplemental polymer applied by immersion - no pressure

Test conditions: 800 psi, 34,300 ppm NaCl, pH 5.5.

E. PROGRAM SUMMARY

During the course of this investigation, the MSI-400 membrane barrier layer was optimized for the desalination of seawater. During the laboratory phase, the significant variables of membrane barrier layer formation were investigated. The best results that were achieved was 16.2 GFD with 99.3% rejection when tested on a feedwater containing about 35,000 mg/l of sodium chloride at 800 psig and 75°F. The subsequent phase developed both procedures and barrier layer formation variables on a continuous interfacial applicator. The best repeatable performance obtained with this equipment on selected samples was 17 GFD and 99% rejection with a feedwater as described above. It is emphasized that these results were obtained on selected samples and are not representative of the entire sheet or roll of membrane.

Due to imperfections in the fabric carrier materials, The porous substrates contained imperfections which were subsequently transmitted to the membrane barrier layer under pressure. This results in a collapse of the membrane barrier layer and the consequent loss of rejection in that region of the membrane. With the present state of fabric carrier material development, the approach to solving this problem has been the repair of imperfections prior to incorporation of the membrane into spiral wound elements.

Fabrication techniques were developed to incorporate the membrane into spiral wound elements with nominal

dimensions of 2 inch diameter and 12 inches long. The membrane repair procedure was to identify imperfections over a light table and to glue that area on the fabric carrier material side of the membrane immediately prior to incorporation into an element. This procedure had been successful in fabrication of low pressure (250 psig) brackish water elements. However, under the elevated pressure (800 psig) required for seawater desalination, problems were encountered. Post-mortem examination of elements which had been tested at 800 psig with dye in the sump, revealed that feedwater was able to pass into the imperfection in the porous substrate and travel in a tortuous path through the porous support and eventually emerge beyond the perimeter of the glue patch on the fabric carrier material.

In conclusion, the membrane barrier layer developed under this contract is capable of single stage desalination of seawater. However, the lack of high quality fabric carrier materials remain the major impediment to large scale production of a single stage composite membrane with acceptable manufacturing yields.

III. MSI-500 MEMBRANE SERIES

In the continuing pursuit of a high performance, chlorine stable membrane, various polymers and polymerization techniques have been investigated. Among these are the NS-100, PA-100, PA-300, and MSI-400. All of these have commercially viable properties of flux and rejection in addition to improvements in capabilities to operate over a wider pH range, to tolerate higher temperatures, and to be essentially immune to biological attack. However, these membranes are susceptible to attack from chlorinated feedwaters.

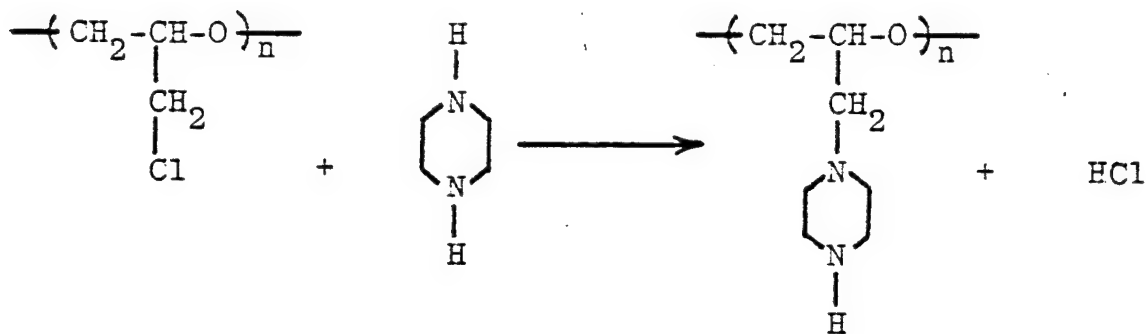
$$\begin{array}{ccc}
 \text{---}(\text{CH}_2\text{---CH---O})_n\text{---} & + & \text{Cl---C(=O)---C}_6\text{H}_4\text{---C(=O)---Cl} \\
 | & & \text{ISOPHTHALOYL} \\
 \text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2 & & \text{CHLORIDE} \\
 \text{EPIAMINE} & & \downarrow \\
 \begin{array}{c}
 \text{---}(\text{CH}_2\text{---CH---O})_n\text{---} \\
 | \\
 \text{CH}_2 \\
 | \\
 \text{N---CH}_2\text{CH}_2\text{NH---C(=O)---C}_6\text{H}_4\text{---C(=O)---NH---} \\
 | \\
 \text{O=C---}
 \end{array} & & \text{PA-300 BARRIER}
 \end{array}$$

54

been hypothesized that the susceptibility to attack by chlorinated feedwaters is attributable to the fact that a secondary amine remains in the backbone of the barrier polymer. This secondary amine is subject to N-chlorination and subsequent depolymerization of the barrier polymer with resultant loss of desalination properties.

Work performed at Membrane Systems and by others, indicates that a barrier polymer formed from the interfacial condensation of piperazine and isophthaloyl chloride is insensitive to chlorinated feedwater attack. This is believed to be due to the fact that the secondary amines in piperazine are converted to tertiary amides during the interfacial condensation and are thereby rendered insensitive to N-chlorination and depolymerization. While this membrane retains good properties in regard to higher operating temperatures, a greater range of pH tolerance and biological immunity than classical asymmetric cellulose acetate membranes, the flux and rejection characteristics are marginal for commercial application.

The objective of a program under OWRT Contract No. 14-34-0001-8510, was the development of a new chlorine resistant reverse osmosis membrane for brackish water applications. The approach used involved the synthesis of a polyamine by the bimolecular nucleophilic substitution of a polyepichlorohydrin backbone with the difunctional secondary amine, piperazine. It has been designated PEPIAMINE. The reaction is as follows:

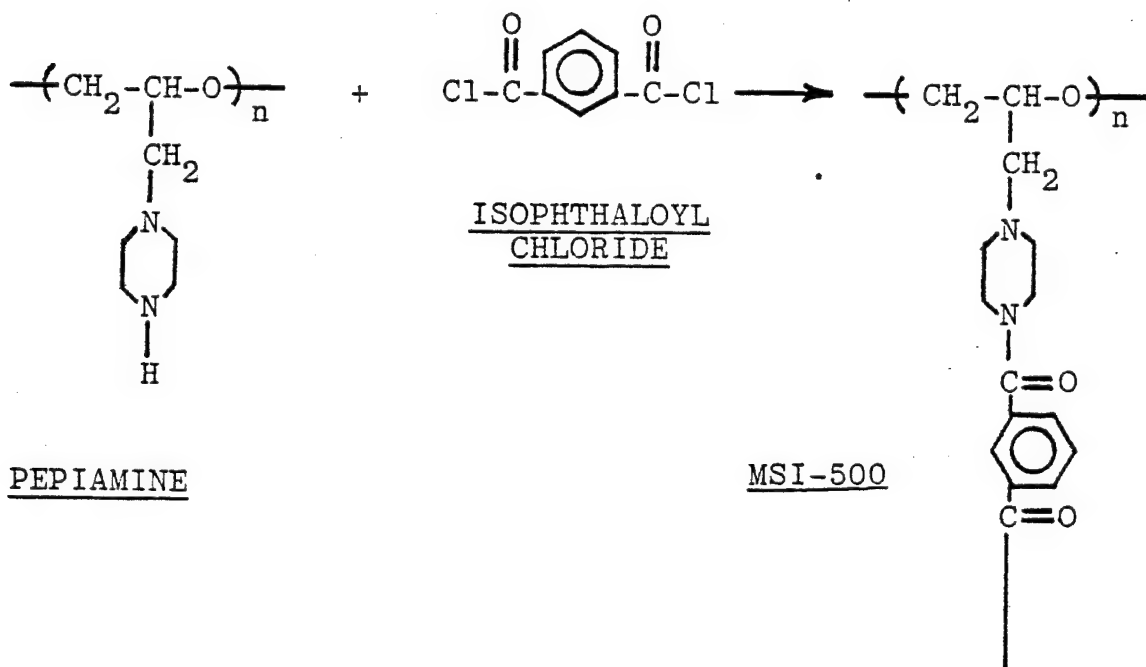


POLYEPICHLORO-
HYDRIN

PIPERAZINE

PEPIAMINE

This polyamine was then interfacially reacted with IPC to form the novel membrane barrier. It has been designated MSI-500. The reaction, which eliminates secondary amines in the cross-link sites, is shown below.

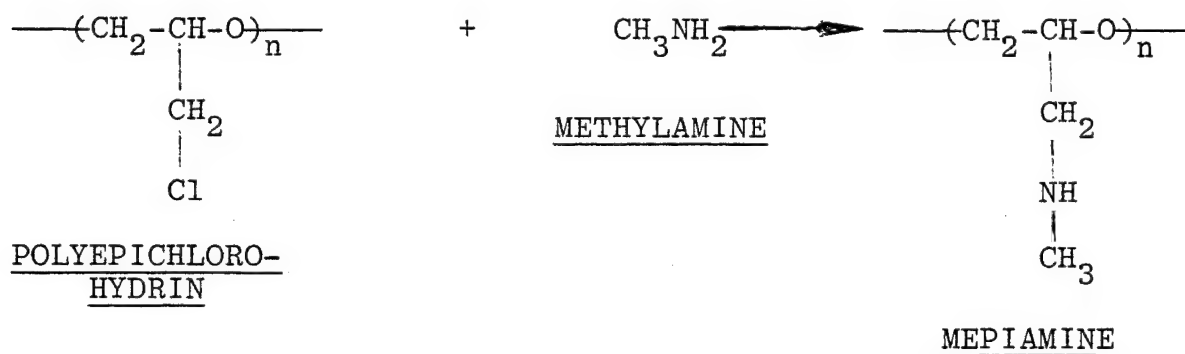


PEPIAMINE

MSI-500

The nominal performance of MSI-500 membrane under brackish water conditions at 250 psig is 96% and 14 GFD.

Another novel secondary polyamine was prepared by reacting methylamine with the low molecular weight ($M_n \sim 2000$) polyepichlorohydrin. It was designated MEPIAMINE. The reaction is as follows:



The best performance of composite membrane prepared with this polyamine was 36% rejection and 54 GFD when tested on a 5000 ppm NaCl feed at 250 psig. Anomalies in the synthesis, elemental analysis, and a further reaction with ethylene dichloride (EDC) led to postulation of a seven membered ring formation rather than full substitution of the polyepichlorohydrin backbone.

None of the synthesized PEPIAMINES gave chlorine stable composite membranes. Membranes prepared with pepiamine and IPC exhibited an initial flux decline with a slight improvement in rejection upon exposure to >1 ppm residual chlorine. Properties slowly degraded over 250 hours of continuous

exposure to chlorine. Membranes prepared with pepiamine reacted with ethylene dichloride prior to reaction with IPC exhibited a slightly increased resistance to chlorine. Due to the poor membrane performance, MEPIAMINE was not tested for chlorine stability.

Two trifunctional acid chlorides, cyanuric chloride and trimesoyl chloride, were investigated as alternative cross-linkers in the interfacial, barrier-forming reaction. Cyanuric chloride gave increased rejection with decreased flux. Trimesoyl chloride was only superficially examined, and gave membranes of less than satisfactory reverse osmosis performance on a 5000 ppm NaCl feed. Neither acid chloride improved the chlorine resistance of the membrane.

In this OWRT Contract (No. 14-34-0001-8523), the PEPIAMINE and MEPIAMINE-acid chloride systems were further investigated in an effort to increase their overall performance for seawater capability.

B. RESEARCH PROGRAM

1. Pepiamine Synthesis

A pepiamine synthesis was undertaken in the final weeks of OWRT Contract No. 14-34-0001-8510 in an effort to duplicate the MSI-500 membrane performance described previously, and also to determine the level of polyamine purification necessary to obtain it. The pepiamine, designated XIII-89, was prepared from a low molecular weight polyepichlorohydrin ($M_n \sim 2000$) and piperazine. The HCl salt of the polyamine was isolated in acetone, and neutralized with an excess of sodium hydroxide. Membranes prepared following the polyamine neutralization step, did not exhibit satisfactory reverse osmosis performance (Table III-1). The polyamine was continuously extracted with a methyl ethyl ketone (MEK)/water azeotropic mixture to remove any residual sodium hydroxide. The semi-solid pepiamine was finally extracted into a water-toluene azeotropic mixture, and this mixture separated to yield an aqueous pepiamine phase and an organic toluene phase. A portion of the pepiamine solution was diluted to the 3.0% control concentration, and a membrane prepared and tested (Table III-1). The results were improved, but remained less than satisfactory. The pepiamine solution was slightly cloudy, and exhibited a faint odor of toluene. The remaining aqueous phase, containing the pepiamine, was evaporated to dryness under vacuum. A portion was again diluted to 3.0% solids, and membranes prepared according to control conditions.

The results are given in Table III-1, and are comparable to the performance of MSI-500 membranes sited previously.

TABLE III-1

REVERSE OSMOSIS PERFORMANCE OF MEMBRANES PREPARED WITH PEPIAMINE XIII-89 AT VARIOUS STAGES OF PURIFICATION. MEMBRANES WERE TESTED AT 250 PSIG ON A 5000 PPM NaCl FEED AND A pH OF 5.

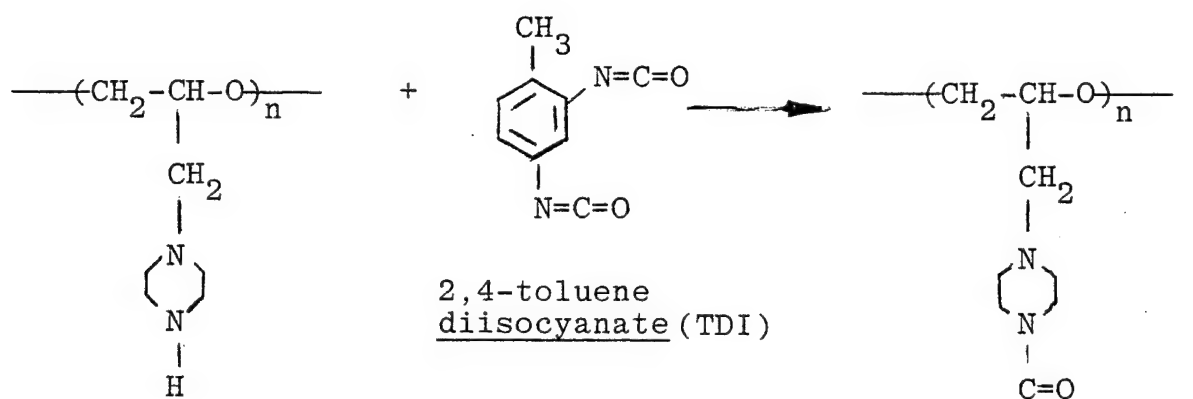
| <u>Purification Stage</u> | <u>*\bar{X} Flux, GFD</u> | <u>*\bar{X} Rejection, %</u> |
|--|--|---|
| Post NaOH neutralization | 4.3 | 66.0 |
| Post MEK/H ₂ O extraction ² | 17.0 | 90.1 |
| Post evaporation of residual solvents | 16.5 | 96.2 |

* \bar{X} is the mean of two samples.

2. MSI-500 Modification for Seawater Capability

Work performed under OWRT Contract No. 14-34-0001-8510 indicated that improved salt rejection (>98% at 250 psig on 5000 ppm NaCl) was possible by substitution of cyanuric chloride for isophthaloyl chloride as the interfacial cross-linking agent in the barrier forming reaction. The flux of these membranes was low (1-3 GFD) however, and in this contract, the MSI-500 system was modified in an effort to increase the overall performance for seawater capability.

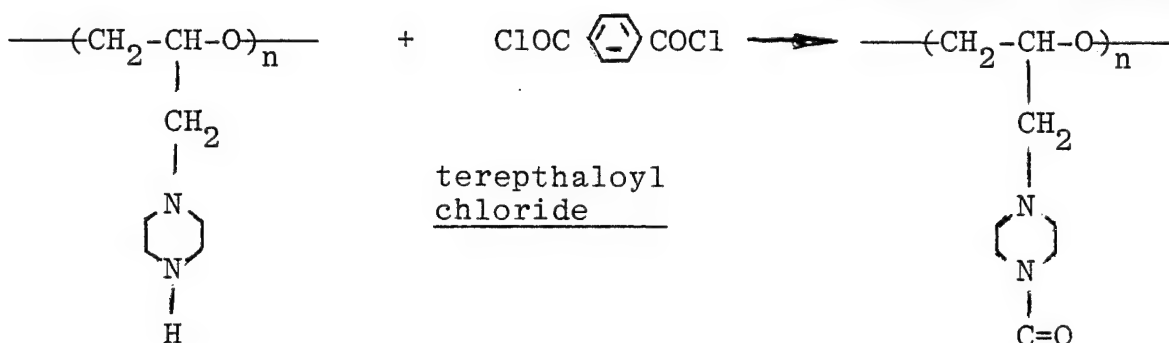
Three additional interfacial crosslinking agents were investigated, and give the following reactions with pepiamine:



2,4-toluene
diisocyanate (TDI)

Pepiamine

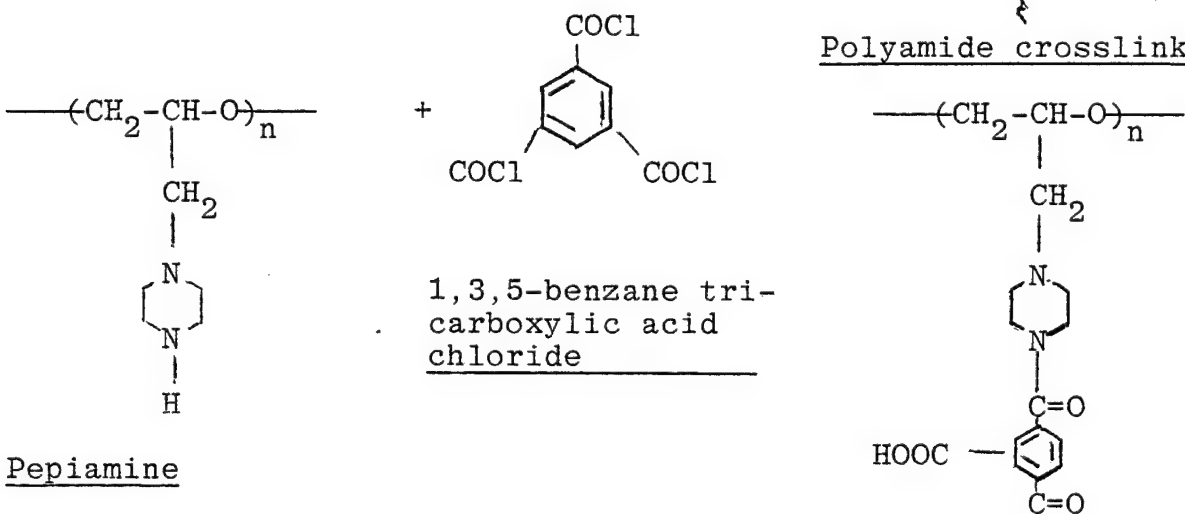
Polyurea crosslink



terephthaloyl
chloride

Pepiamine

Polyamide crosslink



1,3,5-benzene tri-
carboxylic acid
chloride

Pepiamine

polyamide crosslink

1,3,5 benzene tricarboxylic acid chloride (trimesoyl chloride) was cursorily examined in the contract previously mentioned, and gave membranes which exhibited reduced monovalent ion rejection at $\sim 2\frac{1}{2}$ times the flux of comparable MSI-500 membranes. The above reaction is felt to proceed as postulated by Cadotte (Final Report, OWRT Contract No. 14-34-0001-6521).

Membranes were prepared with varying IPC or alternative interfacial crosslinker concentrations. All other membrane formation parameters were held constant. The membranes were evaluated on a 5000 ppm NaCl feed at 250 psig. The results are given in Table III-2. Improved salt rejection was obtained with increased IPC concentrations and with TDI concentrations greater than 1.0%, but with corresponding losses in water flux. Although substantial improvement in the transport properties of membranes prepared with trimesoyl chloride was attained, they remained less than satisfactory for potential seawater desalination. Terephthaloyl chloride offered no advantages over IPC, and was less soluble in the organic solvents commonly employed in the interfacial reactions.

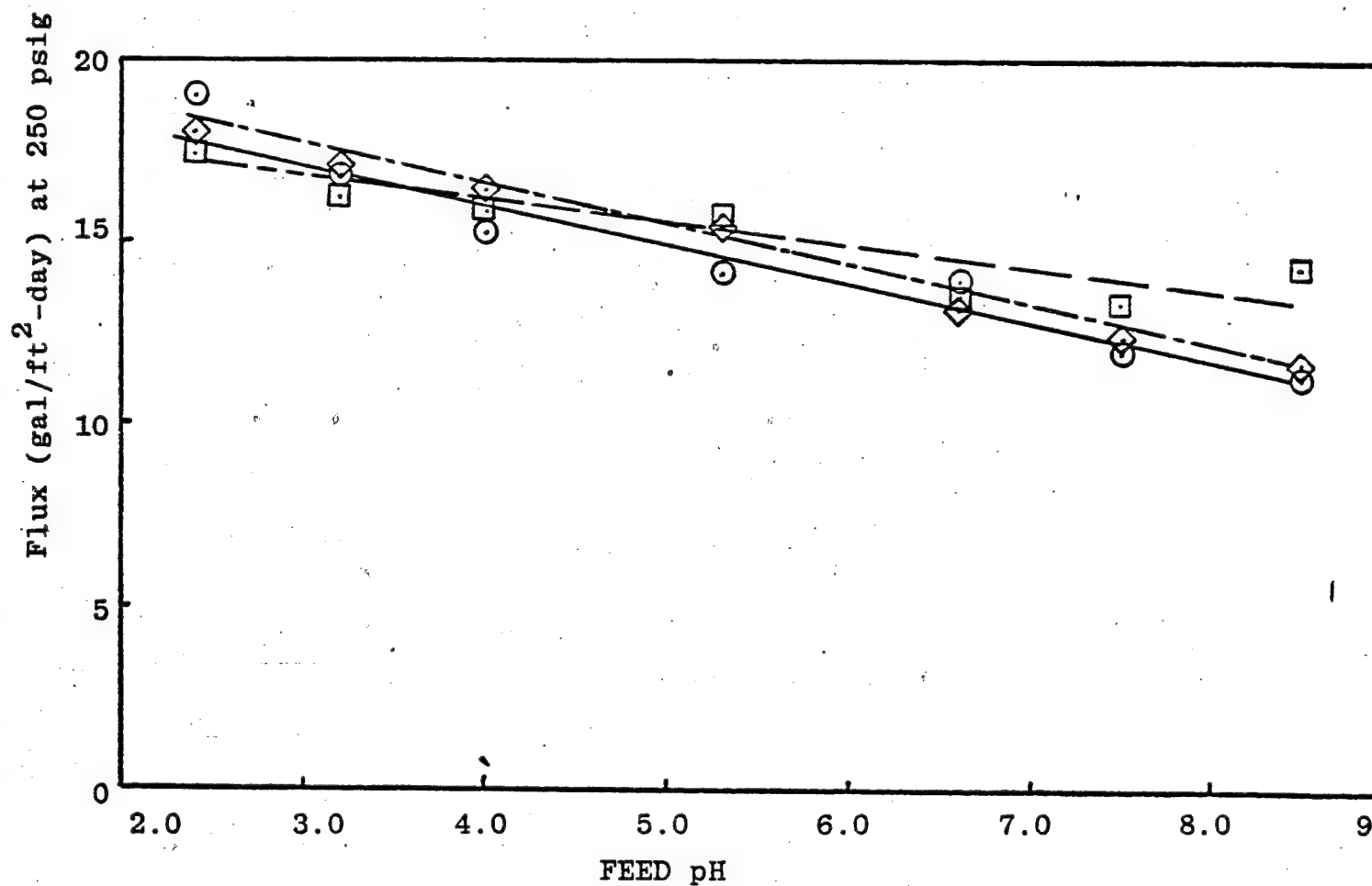
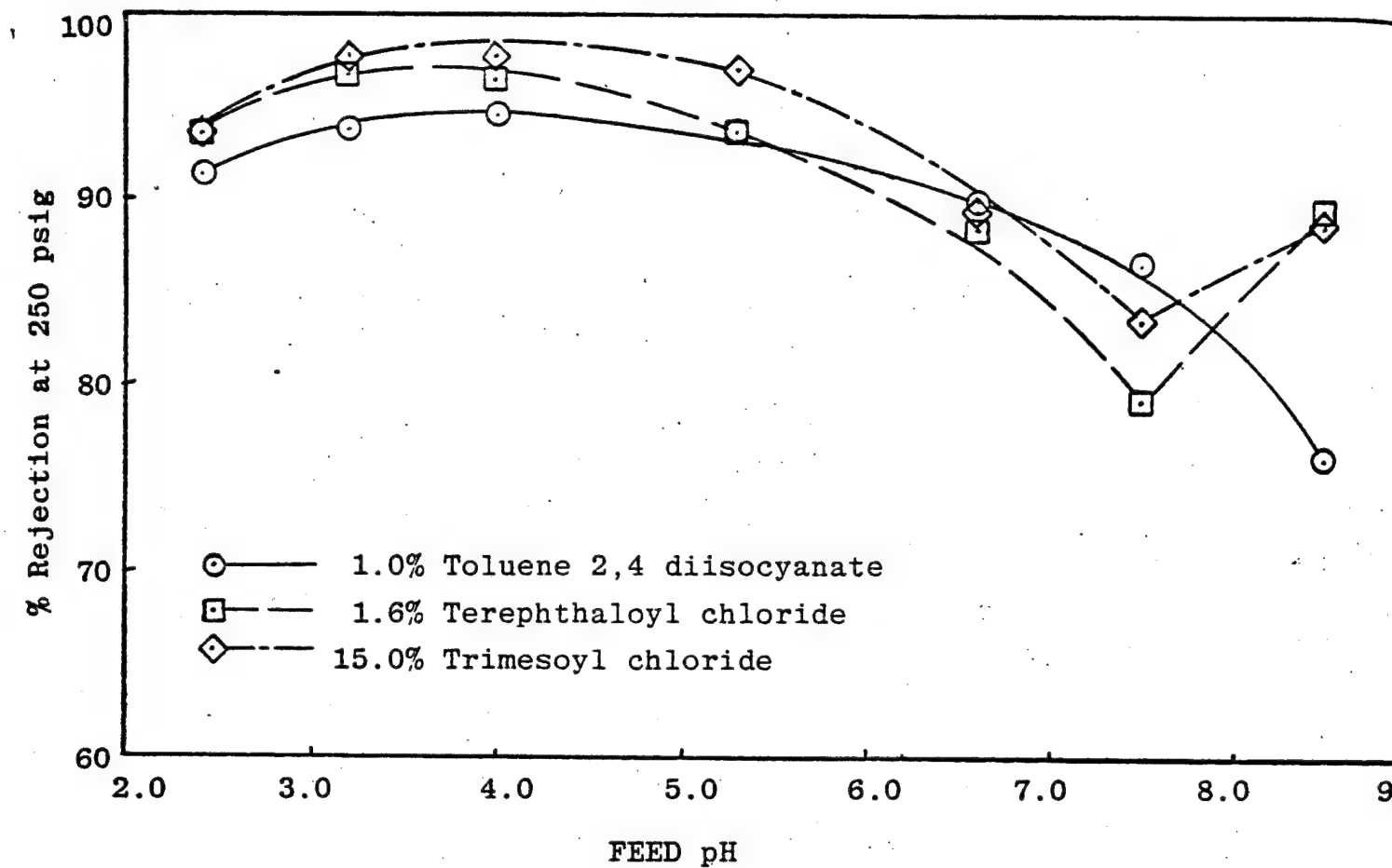
The pH response was determined for membranes prepared at concentrations which resulted in the maximum rejection for the respective interfacial crosslinkers. The results are shown in Figure III-1, and are similar to those obtained for the MSI-500 membrane. The points represent the mean of data obtained as the feed pH was adjusted through the low and high pH range with initial and final pH of 5.3. The percent rejection was

TABLE III-2

REVERSE OSMOSIS PERFORMANCE OF MEMBRANES PREPARED UTILIZING
PEPIAMINE XIII-69 AND VARIOUS ACID CHLORIDES TESTED AT 250 PSIG
ON A 5000 PPM NaCl FEED AT pH 5.

| <u>INTERFACIAL CROSSLINKER</u> | <u>% CONCENTRATION</u> | <u>*\bar{X} FLUX, GFD</u> | <u>*\bar{X} REJECTION, %</u> |
|---|------------------------|--|---|
| Isophthaloyl chloride | 1.0 | 15.0 | 92.6 |
| | 1.6 | 12.0 | 94.5 |
| | 2.0 | 12.9 | 96.0 |
| | 3.0 | 12.2 | 95.7 |
| | 4.0 | 12.4 | 97.0 |
| | 5.0 | 8.9** | 97.5** |
| | 6.0 | 10.0** | 97.4** |
| 2,4-Tolene di- isocyanate | 0.5 | 17.0 | 91.3 |
| | 0.75 | 17.3 | 94.6 |
| | 1.0 | 6.8 | 98.5 |
| | 1.6 | 5.7 | 98.2 |
| | 2.0 | 1.6 | 97.6 |
| | 3.0 | NO FLUX | |
| Terephthaloyl chloride | 0.5 | 23.8** | 78.4** |
| | 1.0 | 13.6 | 95.4 |
| | 1.6 | 13.0 | 95.9 |
| 1,3,5-Benzene tricarboxylic acid chloride (trimesoyl chloride) | 1.0 | 42.6** | 72.8** |
| | 2.0 | 38.6** | 80.5** |
| | 3.0 | 24.9 | 80.8 |
| | 4.0 | 32.3 | 78.0 |
| | 5.0 | 29.2 | 80.2 |
| | 6.0 | 29.7 | 78.8 |
| * mean of four samples unless otherwise indicated | 15.0 | 16.6 | 96.8 |
| ** mean of two samples | 17.5 | 9.7 | 96.7 |

FIGURE III-1



Reverse osmosis performance of membranes prepared with pepiamine and various interfacial crosslinkers as a function of feed pH. Percent rejection determined by titration. 64

determined by mercuric nitrate titration for chloride ion.

Additional membranes were prepared according to the conditions which resulted in the optimum rejection for the respective interfacial crosslinkers. The membranes were tested first on a 5000 ppm NaCl feed at 250 psig and then at 800 psig on a 35,000 ppm NaCl feed. The results of initial tests are contained in Table III-3. As can be seen from the table, the brackish water performance of all of the membranes was substandard in comparison to the results previously stated (Table III-2). These substandard results were repeated in terms of seawater when tested under the seawater conditions. An examination of the tested membranes revealed a combination of defects; particulates in the barrier, support defects, and defects imparted by the test cell (notably o-ring damage to membrane). Additional membranes were prepared with TDI at the selected concentration. Special attention was paid to eliminate the above problems in preparation and testing of the membranes. The results are given in Table III-3, and show substantially improved rejection under both brackish and seawater conditions. Several membrane samples exhibited rejections $\geq 99\%$, with one sample attaining a 99.4% salt rejection at 800 psig under seawater conditions. Further improvement in membrane properties may be possible, however, time limitations precluded further investigation in this program. The membranes in the alternative crosslinker study were prepared utilizing conditions which resulted in the optimum brackish water

TABLE III-3

REVERSE OSMOSIS PERFORMANCE OF MEMBRANES PREPARED WITH PEPIAMINE AND VARIOUS INTERFACIAL CROSSLINKING AGENTS, AND TESTED UNDER BRACKISH (5000 PPM NaCl, 250 PSIG) AND SEAWATER (35,000 PPM NaCl; 800 PSIG) CONDITIONS.

| <u>Crosslinking Agent</u> | <u>% Concen- tration</u> | <u>No. of Samples</u> | <u>\bar{X} Flux, GFD</u> <u>Brack.</u> | <u>Sea.</u> | <u>\bar{X} % Rej.</u> <u>Brack.</u> | <u>Sea.</u> |
|--|------------------------------|---------------------------|--|-------------|---|-------------|
| Isophthaloyl chloride | 1.6 | 4 | 16.3 | 23.4 | 92.4 | 91.0 |
| | 5.0 | 2 | 14.8 | 21.6 | 91.0 | 94.0 |
| Toluene 2,4 diisocyanate | 1.0 | 4 | 13.2 | 16.3 | 90.4 | 88.4 |
| Terephthaloyl chloride | 1.6 | 2 | 12.8 | 19.7 | 97.6 | 92.6 |
| Cyanuric chloride | 0.3 | 4 | 2.0 | 4.4 | 96.0 | 97.4 |
| 1,3,5-Benzene tricarboxylic acid chloride (trimesoyl chloride) | 15.0 | 4 | 17.6 | 30.8 | 90.4 | 89.6 |
| Repeat toluene 2,4-diisocyanate (improved handling) | 1.0 | 6/8 | 5.1 | 6.1 | 98.6 | 98.2 |

membrane performance. An optimizing scheme (i.e., Self Directing Optimization) such as that employed for optimization of the brackish water membrane would likely yield a further improvement in the seawater membrane. In addition, the as yet unexplored area of solution additives such as acid acceptors and wetting agents might also improve both the brackish and seawater membrane performance.

3. Mepiamine Synthesis and Evaluation

In addition to the piperazine/polyepichlorohydrin condensate, pepiamine, a methylamine substituted polyepichlorohydrin prepolymer synthesis was undertaken under OWRT Contract No. 14-34-0001-8510. The investigation of mepiamine was intended to increase the overall view of the tertiary polyamides, from their synthesis to membrane performance in a chlorinated feed. A water soluble, polymeric product was obtained, which gave a thin film when reacted interfacially with IPC. However, membranes prepared with this polyamine at various IPC concentrations showed poor rejection characteristics when tested on a 5000 ppm NaCl feed at 250 psig. Anomalies in the elemental analysis and infrared spectrum, as well as the relative limited reactivity with ethylene dichloride (in comparison to pepiamine) led to a hypothesis of the formation of seven membered rings rather than complete methylamine substitution of the polyepichlorohydrin backbone. The proposed solution to the problem was to change the reaction conditions to those more favorable to the amine substitution rather than the ring closure. It was postulated that the

reaction should be run in a solvent mutually compatible to the polyepichlorohydrin and methylamine. In accordance with this proposal, two mepiamine syntheses were undertaken in this program, and will be described separately.

The first mepiamine, designated XIII-100, was prepared utilizing a low molecular weight ($M_n \sim 2000$) polyepichlorohydrin. The methylamine was distilled from an aqueous solution into a dimethylformamide (DMF) solution containing the polyepichlorohydrin. The reaction was run in a pressure vessel at $\sim 120^\circ\text{C}$ for 69 hours. The reaction mixture was evaporated to dryness to remove the residual methylamine and DMF, and the resulting polyamine hydrochloride was neutralized with aqueous sodium hydroxide. The free polyamine was extracted into acetone to remove the residual sodium hydroxide, and the acetone extract was evaporated to dryness to yield the prepolymer, mepiamine. A small portion of the purified polyamine was sent to Galbraith Laboratories for an elemental analysis, the results of which, will be discussed below. The prepolymer was a water soluble resinous solid that resembled the polyepichlorohydrin precursor. A dilute ($\sim 5\%$ solids) aqueous solution gave a thin film when reacted with IPC, however, the film was very fragile, and only a small amount of bulk polymer was obtained when the two solutions were stirred together. Membranes were prepared interfacially with IPC at different mepiamine concentrations ranging from 3 to 17%. The results are contained in Table III-4. All

TABLE III-4

A COMPARISON OF THE REVERSE OSMOSIS PERFORMANCE OF VARIOUS
MEPIAMINES TESTED AT 250 PSIG ON A 5000 PPM NaCl FEED.

| <u>Mepiamine</u> | <u>Conditions</u> | <u>\bar{X}* Flux, GFD</u> | <u>\bar{X}* % Rej.</u> |
|---|--|--|-------------------------------------|
| XIII-100A (Mn ~2000) sodium hydroxide neutralized | 3% mepiamine conc; 1.6% IPC; 10 min cure | Very high | <10% |
| | 5% mepiamine conc; 1.6% IPC; 10 min cure | Very high | <10% |
| | 17% mepiamine conc; 1.6 IPC; 10 min cure | Very high | <10% |
| XIII-103A (Mn ~100,000) sodium hydroxide neutralized | 3% mepiamine conc; 1.6% IPC; 10 min cure | 66.0 | 33.8 |
| | 3% mepiamine conc; 1.0% TDI; 10 min cure | 55.7 | 45.4 |
| | 3% mepiamine conc; 3.0% TDI; 10 min cure | 58.4 | 33.4 |
| | 3% mepiamine conc; 5.0% TDI; 10 min cure | 49.3 | 38.6 |
| XIII-103A2 (Mn ~100,000) sodium carbonate neutralized | 3% mepiamine conc; 1.6% IPC; 10 min cure | 142.0 | 26.5 |
| | 3% mepiamine conc; 1.0% TDI; 10 min cure | 57.2 | 43.9 |
| | 3% mepiamine conc; 3.0% TDI; 10 min cure | 28.2 | 51.3 |
| | 3% mepiamine conc; 5% TDI; 10 min cure | 5.0 | 65.6 |
| | 5% mepiamine conc; 1.0% TDI; 10 min cure | 30.0 | 47.8 |
| | 3% mepiamine conc; 1.0% TDI; 10 min cure | 21.0** | 58.0** |
| | 3% mepiamine conc; 1.0% TDI; overnight cure | 12.6** | 73.4** |
| | | | |

* \bar{X} is the mean of two samples unless otherwise indicated

** One sample

the membranes were high flux and low rejection (>10%) when tested on a 5000 ppm feed at 250 psig. The viscosity of the polyamine solutions was low, even at 17% solids. An attempt to further react the mepiamine with ethylene dichloride and thereby increase the molecular weight and viscosity was unsuccessful.

The elemental analysis of this mepiamine indicated <80% substitution (based on chlorine content) of the polyepichlorohydrin backbone. Once again, there was a discrepancy between the degree of substitution based on % chlorine in the elemental and that indicated by the % nitrogen. This discrepancy, coupled with other evidence had led previously to the hypothesis of the formation of seven membered rings incorporating adjacent methylene groups with substituted, pendant methylamine. However, there may be a more plausible explanation to account for the observations. Instead of a seven membered ring formation, the polyamine may be cross-linking by the reaction of a substituted methylamine group with a residual chloromethyl group of the polyepichlorohydrin. The two compounds (seven membered ring and crosslinked polyamine) are isomers, that is, they have the same molecular formula, but different molecular structures. This would account for the excellent agreement of the elemental analysis based on this molecular formula. The additional evidence that lends greater credence to this hypothesis (and was overlooked in the formulation of the ring hypothesis) is the presence of

finely divided insoluble material in the mepiamine solution. This solution was prepared after the sample for the elemental analysis was removed.

In the course of the mepiamine workup, another possible degradation route was discovered. Upon neutralization of the HCl salt of the polyamine with sodium hydroxide, a strong methylamine odor was observed, indicating the possible base hydrolysis of the amine. Another mepiamine reaction was conducted to examine the effects of a revised purification scheme, as well as the effects of increased molecular weight on mepiamine membrane performance.

A second mepiamine (XIV-103) reaction was conducted similar to the one previously discussed, but employing a high molecular weight polyepichlorohydrin ($M_n \sim 100,000$). The reaction product was divided into two parts, and one portion was purified by the manner previously described; neutralization of the HCl salt of the mepiamine with sodium hydroxide. Once again, a strong methylamine odor was observed. The other portion was neutralized with sodium carbonate. At high concentrations of sodium carbonate, the odor of methylamine was apparent, but at concentrations less than 20%, it separated from the aqueous solution with no odor of methylamine evolved. The mepiamines were further purified as described previously. Interfacial membranes were prepared with 3% solutions of both polyamines and various concentrations of TDI. The results are contained in Table III-4. As can be

seen from the table, both mepiamines give less than satisfactory reverse osmosis results, and there is no clear distinction as to the better workup. Mepiamine XIII-103A2 appears to exhibit better performance at higher TDI concentrations, but it must be noted that this is an extremely limited sample size, and variation between individual samples is, in some cases, quite large. Additional membranes were prepared utilizing this mepiamine (XIII-103A2) at a higher concentration, and with a longer cure time (one half of the membrane was cured for the normal time). The results are given in Table III-4. The membrane prepared with the longer cure time showed a significantly improved performance over any mepiamine membrane to date. Due to time limitations, this test was not repeated. There was no significant improvement in membrane properties with the higher molecular weight mepiamine, based on the limited sample size previously mentioned, and comparing the results of membranes prepared under similar conditions.

C. PROGRAM SUMMARY

In the course of this program, the MSI-500 system was modified in an effort to increase the overall performance for seawater capability. Membranes were prepared with varying IPC and alternative interfacial crosslinker concentrations, and tested on a brackish water feed at 250 psig. Substantial improvement was obtained in the monovalent ion, brackish water performance of membranes prepared with trimesoyl chloride. The reverse osmosis performance as a function of feed pH was determined at selected concentrations of the various interfacial crosslinkers. The results are similar to those obtained for the MSI-500 membrane. Membranes were prepared at the selected concentrations of the various crosslinkers and tested first under brackish, and then seawater conditions. Initial results were poor, and were attributed to a combination of defects; particulates in the membrane barrier, support defects and test cell damage. Further tests were conducted employing the most promising candidate crosslinker, TDI. Several samples gave favorable results under seawater conditions, with one sample attaining a 99.4% salt rejection at 800 psig. Further improvement in membrane properties may be possible through the use of an optimizing simplex, such as the SDO (Self Directing Optimization), for seawater membranes. Additional interfacial crosslinkers, as well as acid acceptors and wetting agents might also yield improved membrane performance.

In addition to the above work, a secondary polyamine (pepiamine) resulting from the reaction between polyepichlorohydrin and piperazine, was synthesized which successfully duplicated the favorable results obtained with a similar pepaimine prepared under OWRT Contract No. 14-34-0001-8510. The membrane performance was evaluated at various stages in the purification procedure, and it appears that all the purification steps outlined previously (Final Report OWRT Contract No. 14-34-0001-8510) and briefly described in this report, are necessary to attain >95% rejection and ≥ 14 GFD at 250 psig on a 5000 ppm NaCl feed.

Another novel secondary polyamine, mepiamine, was prepared by reacting methylamine with polyepichlorohydrin. Anomalies in the synthesis, elemental analysis and a further reaction with ethylene dichloride had led (OWRT Contract No. 14-34-0001-8510) to postulation of seven membered ring formation rather than full substitution of the polyepichlorohydrin backbone. However, crosslinking by the reaction of a substituted methylamine with a residual chloromethyl group is felt to be a more plausible explanation to account for the observations. Another possible degradation route is that of base hydrolysis with sodium hydroxide in the neutralization step. However, there was no significant difference in the performance of membranes prepared with a mepiamine neutralized

under milder conditions with sodium carbonate. A membrane prepared with a longer cure time gave a significantly improved rejection (>70% vs. 58%) over an identical membrane sample given substantially less cure.

IV. MSI-600 MEMBRANE SERIES

A. INTRODUCTION

Much of the initial development and successful application of reverse osmosis for water desalination has been based on the use of asymmetric cellulose acetate membrane. Considerable work has been devoted to improving these membrane and while they have been used judiciously in many applications, they have not exhibited the desired thermal, chemical or biological stability. Increased stability in these areas have been achieved with both asymmetric and composite polyamides, but these membranes are subject to attack by residual chlorine in feedwaters. Consequently, alternative polymers are under investigation to provide membranes with increased thermal, chemical and biological stability as well as inertness to chlorinated feedwaters.

Under the OWRT Contract No. 14-34-0001-8510, polyimides were first developed as porous supports for thin film composite membranes. As a part of that effort, it was found that polyimide forms an anisotropic hydrophilic membrane with a surface porosity fine enough to exhibit some semipermeability to sodium chloride solutions. From these observations was born the concept of asymmetric polyimide membranes composed of a classical barrier layer and swollen substructure.

Typically, polyimides are the product of a reaction between a dianhydride and a diamine to produce a soluble polyamic acid, which is thermally converted to a polyimide by the elimination of water. The fully imidized polyimides are

distinguished from the poly(amide) imides in that the latter are formed from an aromatic anhydride containing a carboxyl or acid chloride group.

Polyimides have been reported to retain mechanical properties up to 500°F in air. However, nothing is known about the retention of desalination or filtration properties at high temperatures. The polymer is resistant to a number of solvents such as aromatics, aliphatics, chlorinated hydrocarbons, ketones, esters and alcohols. While it is sensitive to extremes of acidity and alkalinity, the polymer should be impervious to the pH encountered in feedwaters for desalination. Polyimides are reported to be completely resistant to fungus attack. Strong oxidizing agents such as a concentrated solution of sodium hypochlorite will attack polyimides. This is also the case with cellulose acetate and it has been demonstrated that cellulose acetate is capable of operating for long periods of time in concentrations in the mg/l range of residual chlorine. It is possible that this is also true for polyimides.

Since the fully imidized polyimide polymers have shown such interesting properties, it was the goal of that endeavor to develop an asymmetric polyimide membrane having acceptable resistance to residual chlorine, and chemical, biological and thermal stabilities superior to those of cellulose acetate. That program yielded a polyimide product exhibiting good

brackish water desalting capability at modest fluxes. The work currently reported is an extension of that program. The overall goal of continued efforts has been to establish formulation and fabrication conditions for asymmetric polyimide membranes that provide competitive fluxes and compaction resistance for seawater demineralization.

B. RESEARCH PROGRAM

The work has been broken into categories of formulation and casting conditions. The experiments within categories were conducted on a cause and effect basis in terms of resultant membrane properties to identify key variables and quantify them to the extent possible. Specifically, formulation variables included studies of alternative solvent systems, polymer content and solution modifiers. Fabrication variables included casting conditions of speed and quench bath temperature and carrier fabric influence. In addition, membrane performance as a function of feed pH was investigated.

1. Polymer Types

Polyimides (PI) are typically prepared from condensation of diamines or diisocyanates with dianhydrides. There are many possible polyimides depending on the nature and molecular weight of the reactants used. Polyimides with a high proportion of polar groups in the repeating structure are hydrophilic, and are thus attractive candidates for semipermeable membranes. Of commercially available polyimides tested to date, the material from Upjohn, #2080, has proved most satisfactory in this function. This PI is derived from copolymerization of benzophenone tetracarboxylic dianhydride (BTDA) with tolylene-2,4-diisocyanate (TDI) and methylene diisocyanate (MDI). This provides short chain or aromatic groups combined with substantial keto and nitrogen groups per repeating molecular unit resulting in about 1/3 hydrophilic groups in the fully imidized

product. Other polyimides are available from DuPont, Rhodia, Rhone-Poulenc and Ciba-Geigy. Examples tested were either low molecular weight or too hydrophobic. One sample from Ciba-Geigy, #XU-218, was marginal in water transport capability and contained less than 20% hydrophilic groups. Standard 20% formulations in current use gave dense films; however, by subsequently adding a substantial amount of isopropanol as a pore former (several percent), a membrane of sufficient asymmetry was cast which exhibited transport properties of 92.6% rejection at 12.4 gal/ft²-day under 0.5% NaCl at 400 psi applied pressure. The Ciba-Geigy polymer then gives a tighter, less well defined, asymmetric structure than that from Upjohn so far. So its use was not further pursued. These results point out experimental differences between polyimide polymers, which suggests that ultimately, a custom synthesized polyimide containing a high fraction of polar groups may be most adaptable to reverse osmosis application.

Experiments were conducted to compare membranes prepared with two forms of polyimide from Upjohn. One form, 2080, was a 200 mesh powder and the other was a solution in DMF, 2080D. Several runs were made using formulations containing concentrated HCl and LiNO₃ solution modifiers. The results are shown in Table IV-1.

TABLE IV-1

| <u>Solution Modifier (0.25%)</u> | <u>PI Type</u> | <u>% Rejection (Cl⁻)</u> | <u>Water Flux (gal/ft²-day)</u> |
|--------------------------------------|------------------|---|--|
| LiNO ₃ | 2080 + 2080D | 94.7 | 12.1 |
| LiNO ₃ | 2080 powder only | 93.7 | 11.8 |
| HCl (36%) | 2080 + 2080D | 95.6 | 10.4 |
| HCl (36%) | 2080 powder only | 97.4 | 12.8 |

Membrane properties as function of polyimide source and solution modifier type. Test conditions: 400 psi applied pressure, 5000 ppm NaCl, pH 5.5.

These data indicate no advantage to one form of PI over the other. There is a disadvantage with the solution form when used with the lithium salt in that mixing time was much longer due to unavailability of fresh DMF to dissolve the salt. Also, since excellent transport properties were attained with the HCl/PI powder only combination, exclusive use of the powder form is most expedient.

2. Formulation Studies

Solution modifiers are used to alter the solvent exchange mechanism during gelation of the freshly cast film. Gel structure and asymmetry are significantly affected by this mechanism. Non-solvents, pore formers, and swelling agents are examples of such solution modifiers. The non-solvent, dioxane, functions as a precipitating agent to insure a good barrier layer as it is absorbed by the quench bath. Other materials may promote gel asymmetry by imbibing water to form.

a swollen substructure. Several families of solution modifiers have been currently tested at a 1/4-3/8% level for effect on polyimide membranes. These were selected from a wide variety of water soluble organic solvents, acids, and salts. Casting conditions used 0.25 in/sec nitrogen velocity, speed 0.5 to 1.0 ft/min and quench bath temperature variation from 15° - 31°C. All membrane was cast onto Pellon 6100 non-woven polyester fabric. Results are shown in Table IV-2. These results represent the average of several casting runs. During the course of each run, it was found that there were optimum speeds for maximum quench line stability. The optimum varied with the casting solution, quench bath temperature, and membrane thickness. Such variables could be overriding factors affecting the transport properties if not controlled. The result was that there were few dramatic differences in membranes prepared from the different formulations when they were successfully cast.

The effect that the casting conditions can override the formulation is offset partially by the fact that some formulations are consistently easier to cast than others. The incorporation of additives like HCl or LiNO_3 , and to a lesser extent, acetone and the alcohols had a stabilizing effect allowing wider tolerances in casting conditions to achieve successful results.

TABLE IV-2

| Solution Modifier | 15° | | 22° | | 25° | | 31° | |
|---|--------|-------|---------|-------|--------|-------|--------|-------|
| | Flux | Rej. | Flux | Rej. | Flux | Rej. | Flux | Rej. |
| None | | | 11.4gfd | 93.4% | 9.6gfd | 95.1% | 4.9gfd | 97.7% |
| LiNO ₃ | | | 12.1 | 94.7 | 8.4 | 96.2 | 4.9 | 97.5 |
| KI | | | 8.3 | 95.6 | 7.7 | 96.3 | 6.3 | 97.1 |
| Isopropanol | 9.5gfd | 96.1% | 12.7 | 94.9 | 14.4 | 92.1 | 5.1 | 97.6 |
| HCl | 10.4 | 95.6 | 8.9 | 95.6 | 6.2 | 97.6 | 7.4 | 96.3 |
| Methanol | 6.1 | 95.4 | 9.6 | 95.4 | 9.3 | 96.2 | | |
| Tetrahydrofuran | | | | | 9.9 | 95.5 | | |
| Ethanol | | | | | 8.2 | 98.2 | | |
| Diacetone | | | | | | | | |
| Alcohol | | | | | 14.8 | 89.6 | | |
| Acetone | | | | | 13.5 | 94.0 | | |
| H ₂ SO ₄ | | | | | 8.1 | 90.2 | | |
| HCO ₂ H | | | | | 5.3 | 85.0 | | |
| CaCl ₂ (Sat) | | | | | 9.3 | 94.5 | | |
| S ₂ Cl ₂ | | | | | 7.4 | 95.0 | | |
| HC ₂ H ₃ O ₂ | | | | | 6.8 | 95.4 | | |
| Glycol | | | | | 7.0 | 93.2 | | |
| Methylcellosolve | | | | | | | | |
| Acetate | | | | | 10.8 | 84.6 | | |

Effects of solution modifiers and quench bath temperature on transport properties of asymmetric polyimide membranes. Test conditions: 5000 ppm NaCl, pH 5.5, 400 psi applied pressure.

2.1. Alternative Solvents and Polymer Content Variation

Three solvents were tested in substitution for DMF, established as a good solvent in initial work. These were dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO). In a standard formulation using non-solvent dioxane/solvent ratio = 5, only the DMSO gave membrane with any permselectivity; e.g., 86.5% rejection at 2.1 GFD under test conditions of 400 psi applied pressure on 5000 ppm NaCl feed. The choice of solvent and probably its content, then showed a dramatic influence on resultant membrane properties. NMP gave very high fluxes, so was taken as the most promising alternate to DMF.

A study was then conducted between dioxane/solvent ratio and polymer content, using as solvents, DMF and NMP. The results are shown in the Table IV-3 matrix.

TABLE IV-3
DIOXANE/DMF RATIO

| % Solids | 3 | | 4 | | 5 | |
|----------|------------|---------|------------|---------|----------|---------|
| | Flux | Rej. | Flux | Rej. | Flux | Rej. |
| 22% | 9.4 gfd | @ 91.4% | 7.2 gfd | @ 91.8% | 8.1 gfd | @ 94.2% |
| 20% | Untestable | | 10.2 gfd | @ 90.4% | 11.8 gfd | @ 95.7% |
| 18% | Untestable | | Untestable | | 18.1 gfd | @ 85.2% |

| % Solids | 3 | | 4 | | 5 | |
|----------|------------|---------|------------|---------|------------|---------|
| | Flux | Rej. | Flux | Rej. | Flux | Rej. |
| 22% | 15.4 gfd | @ 83.3% | 8.4 gfd | @ 84.7% | 13.7 gfd | @ 87.3% |
| 20% | Untestable | | 14.0 gfd | @ 86.8% | Untestable | |
| 18% | Untestable | | Untestable | | 11.7 gfd | @ 84.1% |

Survey of polyimide membrane properties as functions of solids content, solvent type and content. Test conditions: 5000 ppm NaCl, pH 5.5, 400 psi applied pressure

An advantage of the NMP was its superior solvent characteristics. Formulations that previously took a week of ball mill mixing with DMF, required approximately 48 hours with NMP. This series points out an advantageous trend of higher solids content at higher dioxane/NMP ratios, i.e., 22% polymer and ratios greater than 5. To this end, a set of formulations containing approximately 0.5% HCl as pore former, was cast under conditions of 45-50 ft/hr into 25°C water. Table IV-4 shows admirable membrane performance with a dioxane/NMP ratio of 6.

TABLE IV-4

| <u>D/NMP Ratio</u> | <u>Casting Run No.</u> | <u>Flux, GFD</u> | <u>% Rejection</u> |
|--------------------|------------------------|------------------|--------------------|
| 6 | 1 | 12.4 | 97.9 |
| 6 | 2 | 6.2 | 97.5 |
| 6 | 3 | 7.7 | 98.4 |
| 6.5 | 4 | 10.1 | 93.9 |
| 6.5 | 5 | 5.7 | 96.1 |
| 6.5 | 6 | 6.8 | 97.7 |

Effects of dioxane/NMP ratio on membrane performance
@ 400 psig, 5000 mg/l NaCl, pH 5.5.

From this table, a significant improvement in transport properties is attainable by incorporation of additives, which provides direction for further improvement through a better understanding of the casting variables.

2.2 Solvent System Variation

The dioxane/DMF ratio was varied from 0.1 - 6.0, and other partially miscible solvents were substituted for dioxane in its function as solution modifier. The only successful test was that of tetrahydrofuran near a saturation level as included in Table IV-5. Others tested in a ratio solvent modifier/DMF of 5 were 4-butyrolactone, sulfolane and morpholine.

TABLE IV-5

| <u>Non-solvent</u> | <u>Non-solvent/DMF</u> | <u>% Rejection (Cl⁻)</u> | <u>Water Flux (gal/ft²-day)</u> |
|--------------------|------------------------|---|--|
| Dioxane | 0.1 | none | — |
| Dioxane | 0.5 | none | — |
| Dioxane | 1.0 | none | — |
| Dioxane | 2.0 | none | — |
| Dioxane | 4.0 | 95.9 | 13.0 |
| Dioxane | 5.0 | 93.4 | 11.4 |
| Dioxane | 6.0 | 95.8 | 11.1 |
| Tetrahydrofuran | 1.0 | 93.6 | 11.6 |

Membrane properties as functions of non-solvent content. Test conditions: 400 psi applied pressure; 5000 ppm NaCl; pH 5.5.

Further work using NMP instead of DMF established a lower limit for the dioxane/NMP ratio of 3, below which dense films were obtained.

3. Casting Conditions

A brief factorial study was conducted between effects of casting speed and quench bath temperature using a standard formulation without additive. The test results are shown in Table IV-5.

TABLE IV-6

| <u>Casting Speed</u> | <u>Quench Bath Temperature</u> | | | |
|----------------------|--------------------------------|-------------|-------------|-------------|
| | <u>15°C</u> | | <u>25°C</u> | |
| | <u>Flux</u> | <u>Rej.</u> | <u>Flux</u> | <u>Rej.</u> |
| 140 ft/hr. | 11.6 gfd | 91.5% | 12.2 gfd | 92.2% |
| 30 ft/hr. | 6.1 | 96.3 | 8.4 | 95.2 |

In these tests, the casting speed is clearly the dominating variable providing a strong trade-off in flux with salt rejection. Further tests were conducted to establish an upper limit of temperature using a casting speed of 50 ft/hr.

TABLE IV-7

| <u>Temperature</u> | <u>Flux (gfd)</u> | <u>Rejection</u> |
|--------------------|-------------------|------------------|
| 25°C | 11.8 | 95.7 |
| 31°C | 6.2 | 95.1 |

It is concluded that about 25°C is the best temperature, and that higher speeds may be used to improve fluxes and provide potentially annealable membrane.

3.1 The Evaporation Step

A study was conducted to evaluate the effects of casting speed and evaporation conditions. The nitrogen velocity during the evaporation step was varied from 0 to 1.8 in/sec and the casting speed was varied from 30 to 100 ft/hr. The test results in Table IV-8 show best membrane properties fell in the range 50-80 ft/hr, again with the general trend toward higher fluxes at higher speeds. The effect of evaporation conditions was overshadowed by other variables and appeared to be of little importance.

TABLE IV-8

| N ₂ Velocity (in/sec) | Casting Speed | | | | | | | |
|-------------------------------------|---------------|------|----------|------|----------|------|-----------|------|
| | 30 ft/hr | | 50 ft/hr | | 80 ft/hr | | 100 ft/hr | |
| | Flux | Rej. | Flux | Rej. | Flux | Rej. | Flux | Rej. |
| 0 | | | 8.0 | 96.6 | 7.2 | 98.4 | | |
| 0.25 | | | 8.5 | 97.2 | 6.1 | 95.4 | | |
| 0.5 | 6.4 | 97.1 | 8.0 | 97.1 | 8.8 | 94.9 | 13.1 | 91.1 |
| 1.0 | 4.0 | 93.9 | | | 11 | 96.1 | | |
| 1.8 | | | 7.4 | 98.6 | 8.2 | 96.5 | | |

Relationship between effects of nitrogen velocity and casting speed on membrane transport properties. Test conditions: 400 psig applied pressure, 5000 ppm NaCl, pH 5.5.

3.2 Solvent System vs. Casting Speed

A set of solution formulations using DMF as solvent was prepared to determine the relative effects of dioxane/DMF ratio and casting speed on membrane transport properties.

The solids content was held constant at 20% while varying the D/DMF between 4 and 5. These formulations were then cast at three speeds using a constant quench temperature of 25°C. The results (Table IV-9) corroborate a strong influence of casting speed on membrane performance, with a useful range at higher D/DMF ratio.

TABLE IV-9

| Casting Speed (Ft/Hr) | D/DMF Ratio | | | |
|--------------------------|-------------|--------------------------------------|------------|--------------------------------------|
| | <u>GFD</u> | <u>⁴</u> <u>% Rej.</u> | <u>GFD</u> | <u>⁵</u> <u>% Rej.</u> |
| 30 | 7.9 | 97.3 | 8.4 | 95.2 |
| 55 | 7.2 | 75.5 | 11.8 | 95.7 |
| 82 | Untestable | | 12.2 | 92.2 |

Relationship between effects of solvent system and casting speed on asymmetric PI membrane properties. Test conditions: 5000 ppm NaCl, 400 psig applied pressure, pH 5.5.

3.3 Pore Former Content, Type and Casting Conditions

A number of experiments were conducted with HCl, acetone and isopropanol as pore formers to measure their relative effectiveness as functions of concentration and casting speed. The results are given in Table IV-10.

TABLE IV-10

| Pore Former | Concentration (%) | Casting Speed (ft/hr) | Flux $\text{ft}^2\text{-day}$ (Gal/ft ² -day) | % Rejection (Cl ⁻) |
|-------------|----------------------|-----------------------------|--|-----------------------------------|
| None | — | 50 | 9.5 | 93.0 |
| HCl | 0.12 | 102 | 12.9 | 97.1 |
| HCl | 0.25 | 61 | 4.5 | 98.6 |
| HCl | 0.25 | 72 | 12.0 | 94.5 |
| HCl | 0.71 | 47 | 11.6 | 97.9 |
| HCl | 2.0 | 47 | Untestable | — |
| Acetone | 0.25 | 45 | 9.7 | 97.6 |
| Acetone | 0.71 | 50 | 10.3 | 97.3 |
| Acetone | 2.0 | 36 | 10.7 | 95.9 |
| Acetone | 2.0 | 82 | 6.5 | 98.3 |
| Isopropanol | 0.25 | 29 | 12.7 | 94.9 |
| Isopropanol | 0.71 | 87 | 6.9 | 97.4 |
| Isopropanol | 0.71 | 50 | 11.9 | 95.7 |
| Isopropanol | 2.0 | 49 | 6.0 | 97.9 |

Membrane properties as functions of pore former type and concentration cast at various speeds. Test conditions: 5000 ppm NaCl, 400 psig applied pressure, pH 5.5.

While good results may be attained using small amounts of HCl, acetone, or low molecular weight alcohols as additives, best reproducibility and experience has been with use of HCl. Comparing the HCl runs in the above table against the blank, it is concluded that its presence allows higher speeds to be used to attain flux improvements while maintaining good salt rejection. This is presumed due to the tightening effect of the additive on the membrane skin during the gelation step.

The amount of additive incorporated in the casting solution can be in the range 0.1 to 1.0% to be effective, with the lower end of the range preferred.

4. Carrier Fabric Evaluation

The slow casting speeds and relatively thin film employed for asymmetric polyimide membranes require that supporting fabrics be fairly dense to avoid "bleed through" prior to gelation, and that the materials be relatively free of protruding fibers and other flaws. Six materials were obtained from Pellon Corporation for evaluation. These were all non-woven polyesters, three of which were manufactured by their associate, Freudenberg in German; and the others were made domestically by Pellon. These were tested using a short path length from knife to gelation bath without an evaporation step. This configuration was necessary because of the nature of allied experiments in progress, so it was not necessarily optimum for PI membranes. However, comparing the runs against one another provided a good survey in terms of bleed through and surface flaws. The results are given in Table IV-11.

TABLE IV-11

| <u>Fabric</u> | <u>Flux (gfd)</u> | <u>Rejection (Cl⁻)</u> | <u>Surface</u> | <u>Observations</u> |
|--------------------|-------------------|-----------------------------------|-------------------|---------------------|
| Pellon 6600 | 5.1 | 93.3 | Protruding fibers | Bleed-thru |
| Pellon 6800 | 5.9 | 92.8 | Protruding fibers | Bleed-thru |
| Pellon 6100 | 10.9 | 92.5 | Protruding fibers | Dense fabric |
| Freudenberg N20130 | 5.8 | 93.7 | Smooth | Bleed-thru |
| Feudenberg N20130 | 5.3 | 89.2 | Smooth | Bleed-thru |
| Freudenberg N20132 | 7.8 | 96.9 | Smooth | Dense fabric |

Support fabric influence on membrane properties.
 Test conditions: 400 psig applied pressure,
 5000 ppm NaCl, pH 5.5.

It was seen that all Pellon fabrics had protruding fibers causing dye uptake at these points and generally poor salt rejection. All looser fabrics regardless of finish, gave poor rejection and flux due to bleed-thru. Only the denser fabrics had no bleed-thru and showed good flux. Of these, the Freudenberg N-20132, was the only one giving good rejection, due to a smooth calendered finish.

5. pH Dependence on Transport Properties

Transport properties versus feed pH was reviewed using a best effort membrane in terms of salt rejection. The membrane samples were left in the test cells at pressure while the pH of the sump was varied from 3 to 10. Figures IV-1 and IV-2 show

% Rejection Based on Conductivity

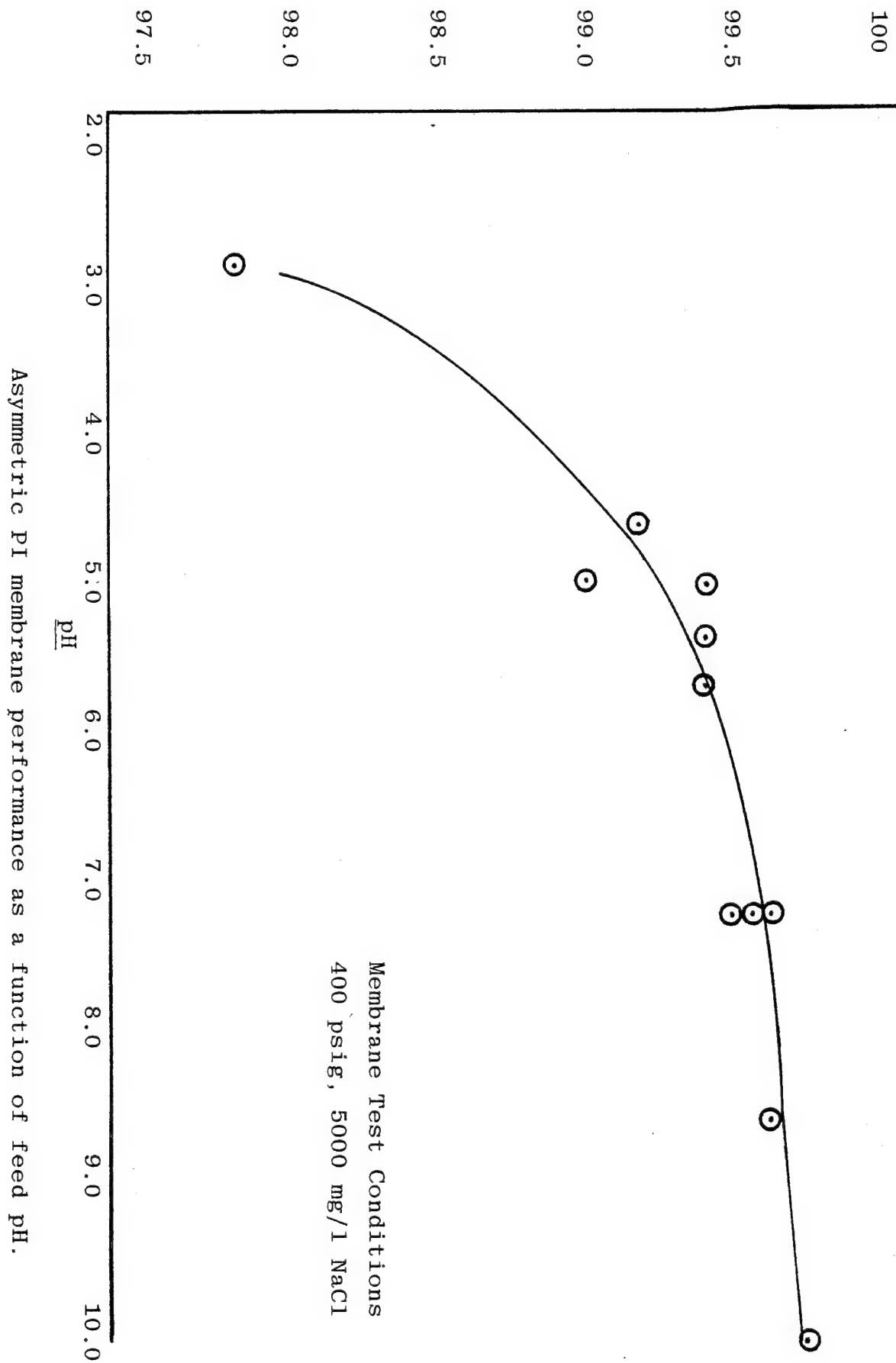
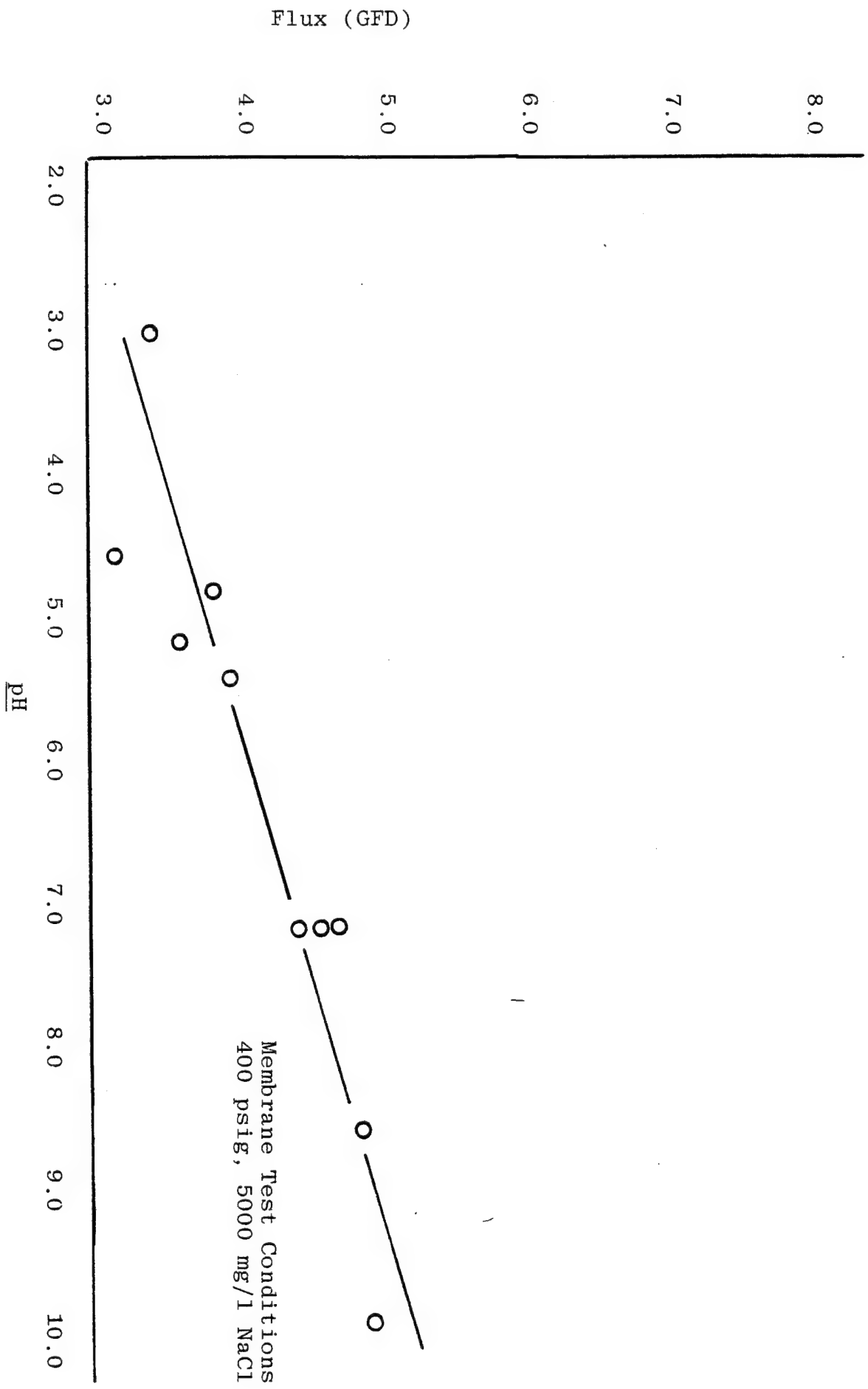


FIGURE IV-1



Asymmetric PI membrane performance as a function of feed pH.

FIGURE IV-2

the increasing trend of both rejection and flux with the increasing feed pH. Note that salt rejections over 99.5% were attained at pH greater than 6.

6. Testing on Seawater

Selected membrane were tested for seawater application at 800 psig applied pressure on a 35,000 ppm NaCl feed at pH 5.5. The results are shown for comparison with the standard brackish water tests at 400 psig applied pressure on a 5000 ppm NaCl feed, pH 5.5.

| N ₂ Velocity (in/sec) | Soln. Modifier (0.25%) | Brackish Water | | Sea Water | |
|-------------------------------------|---------------------------|------------------------------------|------------------------------|------------------------------------|------------------------------|
| | | Flux (gal/ft ² -day) | % Rej. (Cl ⁻) | Flux (gal/ft ² -day) | % Rej. (Cl ⁻) |
| .25 | LiNO ₃ | 12.4 | 95.1 | 9.1 | 95.2 |
| .25 | Methanol | 9.3 | 96.2 | 11.1 | 94.7 |
| .25 | HCl | 8.2 | 98.3 | 9.4 | 96.3 |
| .50 | HCl | 7.3 | 98.7 | 5.3 | 97.6 |
| 1.0 | HCl | 7.4 | 98.7 | 5.8 | 98.4 |

C. PROGRAM SUMMARY

As an extension of a previous contract (OWRT 14-34-0001-8510), an asymmetric membrane of polyimide has been further studied and techniques for its fabrication conditions have resulted in the capability of continuous machine casting in a 1 foot width to give a product with acceptable transport properties. Key variables for flux improvement and quench line stabilization during casting have been defined. Formula-tion variables are non-solvent/solvent ratio, pore former

type and content from which best solvents (DMF and NMP) were established. The key casting variable was speed, where about 1 ft/min was optimum.

These membranes were prepared from commercially available polyimide polymers using known membrane production equipment and carrier fabrics. Properties achieved on brackish water testing were 98-99% salt rejection at 4-13 gal/ft²-day water flux. Properties achieved on seawater testing were 95-98% salt rejection at 5-11 gal/ft²-day. The techniques and information developed and the progress achieved provide a strong basis that remaining improvements can be attained with a reasonable amount of further effort.

V. POROUS SUPPORT

A. INTRODUCTION

In composite membranes, a porous support acts as the substrate for the thin film barrier membrane. The higher the operating pressure under which these membranes are subjected, the more significant become the properties of the porous support. Supports that perform well under brackish water operating pressures (250-400 psig) may be inadequate for seawater desalination conditions (800-1000 psig). Membranes may collapse through the pores under these pressures and/or the substructure may compact causing a decrease in flux. In addition, small mechanical imperfections in the support will allow considerable brine leakage across the membrane at seawater pressures. Research under this contract was aimed at optimizing porous supports for use under the demanding seawater desalting conditions.

B. RESEARCH PROGRAM

1. Support Preparation

In laboratory research of composite membranes, support imperfections can be avoided when cutting samples for testing. However, when producing elements, it is difficult to avoid incorporating various imperfections into the active membrane area. Each imperfection allows a leak in the membrane and drastically reduces the overall salt rejection of the element. These imperfections are due to the physical properties of the fabric carrier material, such as fiber clumps, protruding fibers, wrinkles, splices, warps, etc. Current research in the

area of fabric carrier materials is limited to surveying the fabrics presently available on the market and possible post treatment.

For some time, Pellon 6100 (a non-woven polyester) fabric was used exclusively as a fabric carrier material for porous supports. A problem which was encountered was that of adhesion between the polysulfone and the fabric, prompted several studies in search of the cause. The following variables were investigated.

1. Water Absorption of the Fabric

It was suggested that climatic conditions of high humidity at the time of casting could have caused moisture absorption by the Pellon and thus interfered with adhesion. Various treatments including oven drying the Pellon and casting on hot fabric were tried with little or no improvement in adhesion.

2. Casting Knife Blade and Gap

Three knife blades of different configurations were tried with variations in the knife gap. It was found that casting a support of increased thickness caused greater adhesion problems.

3. Casting Solution Formulation

The original casting solution formulation contained 15% polysulfone (Udel, Union Carbide) 12.5% bis(2-methoxyethyl)ether, and 72.5% N,N'dimethylformamide (DMF).

4. Casting Parameters

Casting speed and distance from knife blade to quench bath were varied with no substantial improvement observed.

5. Backing Material

It was surmised, because a new roll of Pellon 6100 fabric was being used since the adhesion problem occurred, that the particular roll of fabric might be causing the adhesion problem. A new roll of Pellon 6100 and a roll of Eaton-Dikeman 3370 (another non-woven polyester fabric) were tested. The new roll of Pellon 6100 adhered well and the Eaton-Dikeman 3370 exhibited a tenacious bond to the polysulfone although it also contained numerous physical imperfections (pinholes in the polysulfone).

A closer examination of the fabrics showed the problem roll of Pellon which would not adhere to the PS, had a very smooth surface compared to the newer roll that did exhibit adhesion. Through communications with Pellon Corp. representatives, it was suggested that this was probably due to normal variations in the degree of calendering encountered in the production of this fabric.

The Eaton-Dikeman fabric appeared to be much more porous and thus allow better physical contact between the fabric and the casting solution.

Air permeability measurements were made of the various fabrics used. Air permeability is reported as the Frazier Index which is a textile industry standard measured in

ft³ of air/minute/ft² of fabric at 0.5 inches of H₂O. Table V-1 shows these values for the fabrics tested.

TABLE V-1
Frazier Index of Fabrics

| <u>Fabric</u> | | <u>Frazier Index</u> |
|-----------------------|----------|----------------------|
| Pellon 6100 | 1st roll | 1.5 |
| | 2nd roll | 0.5 |
| | 3rd roll | 1.4 |
| Eaton-Dikeman 3361 | 1st roll | 10.0 |
| | 2nd roll | 10.0 |
| Texlon E-0717 | | 4.9 |
| Texlon 0750 | | 10.8 |
| 0715 | | 9.8 |
| Putnam D-601 | | 1.1 |

As can be seen, the Pellon 6100 fabric varies from roll to roll. The 2nd roll, with the lowest Frazier Index (0.5) apparently was more heavily calendered, as suspected, and the cast polysulfone would not adhere to this fabric. The rolls with higher Frazier Indices have good adhesion, however, they also have numerous loose fibers protruding from the surface which cause imperfections in the cast polysulfone.

It can also be noted, that the Eaton-Dikeman fabric is much more porous than the Pellon. This would account for the tenacious bond between the fabric and the cast polysulfone.

A speculation was made that the pinholes seen in cast support were due to trapped air in the fabric, forming bubbles and rising as the casting solution was seeping in.

Various castings were performed in an effort to eliminate the appearance of pinholes. These included the following:

1. Pretreatment of the Fabric

To eliminate the air from the Eaton-Dikeman prior to casting, two efforts were made. In one case, the fabric was coated with an aqueous solution of polyvinylpyrrolidone, then dried. Pinholes were still observed in the cast support.

In another case, the fabric was dipped into DMF immediately prior to the casting blade, however, the support had no integrity and didn't adhere to the fabric.

2. Casting Solution Formulation

An increased solution viscosity would decrease penetration into the fabric. The viscosities of several variations in the polysulfone casting solution were measured (See Table V-2).

TABLE V-2

Casting Solution Viscosities

| <u>Support</u> | <u>% PS</u> | <u>% MC</u> | <u>% Bis</u> | <u>Viscosity (CPS)</u> |
|----------------|-------------|-------------|--------------|----------------------------|
| XVI-9501A | 13 | -- | -- | 120 |
| XVI-95-2A | 15 | -- | -- | 256 |
| XVI-95-3 | 17 | -- | -- | 456 |
| XVII-37-1 | 15 | 12.5 | -- | 384 |
| XIV-137-6 | 17 | 17 | -- | 890 |
| XIV-137-7 | 15 | 15 | -- | 500 |
| XVI-91-1 | 15 | -- | 12.5 | 184 |
| XVI-91-5 | 17 | --- | 12.5 | 476 |

These were all cast using the standard casting parameters. A general decrease in the number of pinholes was observed as the viscosity of the casting solution increased. However, even the highest viscosity solution, consisting of 17% PS and 17% methyl cellosolve (MC), still contained some pinholes. This solution was near the saturation point, however, and the viscosity could not be increased further by addition of either component.

3. Casting Parameters

It was surmised that cutting down the time span which the casting solution has to penetrate the fabric before

quenching would reduce pinhole formation. Increasing the casting speed and decreasing the distance from the knife blade to the quench bath would accomplish this. The casting speed was increased from 7 ft/min to 28 ft/min and the distance to quench, decreased from 8 inches to 2 inches. When combined with the high viscosity casting solution mentioned above, pinholes were reduced significantly.

A further survey of available fabrics turned up some woven polyester fabrics for evaluation. The Frazier Indices are reported in Table V-1. Polysulfone support was cast on these samples. Fiber protrusion, adhesion and pinholes were not problems, however, numerous heat set wrinkles in the Texlon fabric were. Membrane discontinuity was observed, related to the texture of the weave of the Putnam fabric. All the woven fabrics tended to curl when cast upon and created problems both on the casting machine and when rolling into elements.

Polycarbonate (PC) supports were also investigated for potential use as support in composite sea-water membranes. Casting solutions of polycarbonate (Lexan, General Electric) in the solvent DMF were used. The polymer would not go into solution without heating, however, and precipitation would occur within an hour after cooling to room temperature. This presented many problems in handling since the solution had to be filtered, degassed and cast within this time. Additionally, the solutions had a very low viscosity (41 cps). All castings were made on Pellon 6100 fabric but the solutions bled through and the cast supports were very non-uniform in thickness and

properties. The cast support was also very brittle and often flaked off the backing material. Membranes made on the best isolated sections performed comparably to PS, however, there are no technical advantages to using this support when compared to PS.

2. Support Evaluation

The most obvious method of support evaluation is making a membrane on the surface and testing the entire composite for reverse osmosis properties. However, membrane properties themselves vary from sample to sample because of the variables involved in making the membrane. Therefore, the effects of the support on membrane performance are difficult to distinguish from the variation in the membrane itself. An additional disadvantage is the amount of time required to make the test membrane samples on all new support samples.

Of greater advantage, would be a method that allows evaluation of the support sample (before a membrane has been applied). This eliminates the membrane variation and presumably allows a direct correlation between support formation parameters and support properties to be viewed.

An indication of relative surface porosity can be made by measuring the hydraulic permeability of the support at a given pressure. A standard method to measure water permeability was adopted previous to this contract. This method utilized San Diego tap water as a feed and was run at 250 psi. All support samples were oven cured 15 minutes at 100°C prior to testing,

just as they are in the application of a thin film composite reverse osmosis membrane.

This method is adequate for determining large differences between supports. However, rapid fouling as a result of suspended solids in the tap water decreases its usefulness for distinguishing small differences. As support optimization progressed, a more accurate method was developed. Modifications were made by changing to a filtered deionized water feed and reducing the applied pressure to 55 psig to cope with the large fluxes observed. This method produces good reproducibility and was adopted as the new standard indication of support porosity.

Ten repeat castings of the same type of PS support were tested. These supports were made from a casting solution containing 15% PS, 12.5% bis(2-methoxyethyl)ether, and 72.5% DMF. The casting parameters were thought to be identical except for the quench bath temperature. There was no indication that there was a correlation between the variability of the support and quench bath temperature.

The solvent N,N'dimethylformamide (DMF) is known to be very hygroscopic. Even though reagent grade DMF has been used exclusively, it has been suspected that the water content varies from container to container, which could cause variation in the support porosity.

Using a single bottle of DMF, casting solutions were prepared. Half were made adding 1% water and half without. A total of 4 castings of each type were made and the water permeabilities of each are reported in Table V-3.

TABLE V-3

| | <u>Support #</u> | <u>DI-H₂O Flux</u> |
|---------------------|------------------|-------------------------------|
| 0% H ₂ O | XX-64-3 | 1752 |
| | XX-64-9 | 1708 |
| | XX-64-10 | 1870 |
| | XX-60-11 | <u>1672</u> |
| | | $\bar{X} = 1750 \pm 113$ |
| 1% H ₂ O | XX-64-11 | 2580 |
| | XX-64-12 | 2778 |
| | XX-6413 | 2641 |
| | XX-60-13 | <u>2770</u> |
| | | $\bar{X} = 2641 \pm 113$ |

The repeat castings in each group showed excellent reproducibility and a significant increase in water permeability is seen in the 1% water group.

Another physical parameter of the support that will affect membrane performance is the surface pore diameter. This can be measured by the measurement of the rejection of globular shaped proteins. These tests were conducted utilizing a stirred Amicon pressure test cell at 55 psig. Feed solutions were in the range of 500 to 1000 ppm.

Cytochrome C (M.W. 12,500) was the first globular protein investigated. Samples of polysulfone support were selected to determine the effects of casting speed, additives, and fabric carrier material on pore size (Table V-4).

TABLE V-4

Cytochrome C Rejection

| <u>Support #</u> | <u>Additive</u> | <u>% Rejection</u> |
|------------------|-----------------|--------------------|
| XVII-29-6 | No additive | 18 \pm 4.1 |
| IV-25 | 12.5% Bis | 20 \pm 2.9 |

| <u>Support #</u> | <u>Casting Speed</u> | <u>% Rejection</u> |
|------------------|----------------------|--------------------|
| XVII-85-1b | 14 ft/min. | 23 \pm 4.6 |
| SVII-85-1c | 28 | 21 \pm 9.1 |

| <u>Support #</u> | <u>Fabric</u> | <u>% Rejection</u> |
|------------------|--------------------|--------------------|
| XVII-85-1c | Pellon 6100 | 21 \pm 9.1 |
| XVII-85-2 | Eaton-Dikeman 3361 | 19 \pm 4.0 |

A larger globular protein was tried - urease (M.W. 67,000). Various samples of polysulfone support were tested, however, repeatability could not be established. Finally, it was discovered, that the urease in solution was degrading upon being used for testing and thus each subsequent test made with the same solution showed a lower rejection. Continued testing used the feed solution only once and then it was discarded.

Suspecting the the degree of overall porosity is related to the pore size, samples of two PS supports having different water permeabilities were tested. The rejections are listed in Table V-5.

TABLE V-5
Urease Rejection

| <u>Support #</u> | <u>DI-H₂O Flux (GFD)</u> | <u>% Rejection</u> |
|------------------|---|--------------------|
| XX-60-11 | 1660 | 49.7 \pm 6.7 |
| XX-60-13 | 2560 | 42.7 \pm 15.7 |

The ultimate evaluation of a porous support is its performance in a composite reverse osmosis membrane. As mentioned earlier, the performance of small laboratory test samples can be misleading because imperfections can be avoided. In commercial application, these imperfections cannot be avoided and must be considered in the overall evaluation of the fabric. Keeping this in mind, Table V-6 summarizes the best laboratory membranes produced, using polysulfone support on three different backing materials.

TABLE V-6

Composite Membrane Performance on Different Fabric Carrier Materials

| <u>Support #</u> | <u>Fabric</u> | <u>Flux, GFD</u> | <u>% Rejection</u> |
|------------------|--------------------|------------------|--------------------|
| XVII-42-2 | Eaton-Dikeman 3361 | 14.6 | 99.3 |
| XXII-4 | Pellon 6100 | 21.7 | 99.0 |
| XXI-19-4 | Texlon 0715 | 26.6 | 98.6 |

Test Conditions: 35,000 mg/l NaCl, pH 5.5, 800 psig and 75°F.

C. PROGRAM SUMMARY

Porous supports were cast from both polysulfone and polycarbonate. Results with both of these polymers in reverse osmosis test under seawater conditions were about equal. However, preparation of polycarbonate supports is considerably more difficult than the preparation of supports with polysulfone. Since there were no apparent benefits to be gained by pursuing the polycarbonate porous supports, work with this material was suspended.

The polysulfone porous supports were cast on several woven and non-woven fabric carrier materials. From the viewpoint of spiral wound element fabrication as well as support casting, the best results were obtained with Pellon 6100. However, this material is not sufficiently developed at this time to guarantee high manufacturing yields of composite membrane capable of single stage seawater desalination.